Tropical lowland rainforests: rapid recyclers or efficient storers of carbon?

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Abstract

Amazonian rainforests are important systems that vigorously cycle carbon and water at the global and regional scale. However, despite their importance, dynamics of organic matter cycling in tropical rainforests within the global carbon cycle is poorly understood.

New field-based hydrology and geochemistry data is presented from a three-year study (2009-2011) in the pristine rainforest of central Guyana at the northern rim of Amazonia. The study shows that two commonly used satellite- and interpolated-based models to estimate rainfall greatly overestimate and underestimate in the wet and dry season, respectively. This misrepresentation of hydrology at local and regional scales greatly affects our ability to understand and predict the connections and feedbacks between the hydrological and geochemical cycles. River water $\delta^{2}H$ and $\delta^{18}O$ isotopes from peak wet and dry seasons suggest that the majority of rainfall has a residence time of at least one month, which provides regions of water saturated zones for organic matter (OM) to be preserved in deeper rainforest soils ($\Delta^{14}C$ ages of 360-1200 years). In contrast, $\Delta^{14}C$ values of surface soils and dissolved organic matter (DOM) in river water recycle within ~60 years or less. Carbon normalised yields of lignin phenols, used as tracers of vascular plant material, are abundant across the terrestrial-aquatic interface. However, lignin appears to accumulate in river bed sediments. Soil leachate experiments confirm that during mobilisation from soil particulates into the dissolved phase, desorption processes change the composition of lignin biomarker ratios. Surface soil $\delta^{13}C$ signatures show that the majority of carbon is fixed through the C_3 pathway (-26.4 to -32.0‰). However, a strong variability of up to 10‰ in riverine $\delta^{13}C$ of dissolved organic carbon suggests that changing $\delta^{13}C$ of DOC reflects changing contributions of degraded and fresh organic compounds within the total OM pool.

Superimposed on seasonal cycling, short intense rain events cause rapid mobilisation of large amounts of DOC (up to 114 mg/L) that is divided into two main fractions, humic substances and ‘invisible’ DOM, or ‘iDOM’. The latter group is characterised by non UV-absorbing organic compounds of mono- and oligosaccharides, alcohols, aldehydes, ketones and amino sugars. Importantly, iDOM contributes up to 89% to the total river OM pool during peak DOC supply

Declaration

The thesis entitled “Tropical lowland rainforests: rapid recyclers or efficient storers of carbon?” is the result of research undertaken between September 2009 and February 2013. The work is original and no part has been submitted in support of an application for another degree of qualification at this or any other university.

This thesis is the authors own work with the following contributions:

- extraction of TRMM and ERA-Interim reanalysis datasets with assessment of the extracted dataset quality were done by Isabella Bovolo and Nathan Forsythe;
- river discharge rating curves were constructed by Isabella Bovolo;
- water isotopes ($\delta^{18}O$ and $\delta^{2}H$) were analysed by Nikolai Pedentchouk at University of East Anglia, UK;
- Lignin phenols were analysed and integrated at University of California Davis, USA by Peter Hernes and Robert Spencer;
- Nick Chappell assisted with the validation of the hydrology dataset for Blackwater Creek; and
- Andrea Vieth-Hillebrand analysed and integrated the size exclusion chromatography dataset.

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To my family, I love you. To mum and dad, without your support I would not be where I am today. In so many uncountable ways I am and will be eternally grateful. Juliane, my love, my girl, my rock. You are everything to me and you alone know what this has meant to me. I thank you with all my heart.

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Preface

The environment of Earth is actively changing with a multitude of biogeochemical processes that vary in space and time to produce both hot spots and hot moments of elemental cycling. McClain et al. (2003) define biogeochemical hot spots as *"areas that show disproportionately high reaction rates relative to the surrounding area"* and hot moments as *"short periods of time that show disproportionately high reaction rates relative to longer intervening time periods"*. In theory, hot spots and moments can occur at any spatial (molecular to global) or temporal (millisecond to eon) scale (McClain et al., 2003). The key benefit of using this conceptual framework is that it allows the determination of important bioactive elements and reactions that determine the response of an ecosystem to climate and land use changes. The hot spot and moment concept underpins the broader context of new research into the carbon cycle and is the core philosophy used throughout this thesis.

Chapter 1: Introducing the role rainforests and tropical headwaters in the global carbon cycle

The global carbon cycle is a massive area of scientific investigation. When searching for published, peer-reviewed literature on the Web of Knowledge database (www.webofknowledge.com, accessed 12.02.13) there are over 1 million articles relating to carbon and around 70,000 discuss the carbon cycle. This chapter cannot cover all of this detailed knowledge and therefore informs on some of the main principles of the global carbon cycle; where it is stored, the effect of hydrology, over what time scales and human interactions. The chapter then focusses on key issues of carbon cycling in tropical rainforests and the interaction with hydrology that can cause a significant feedback of carbon to the atmosphere and ocean. For more detail on the carbon cycle outside of this thesis McPherson and Sundquist (2009), Schulze (2001) and Wigley and Schimel (2000) are suggested.

1.1 The global carbon cycle

The Earth's carbon is unevenly distributed between terrestrial, oceanic and atmospheric reservoirs (Cole et al., 2007; Falkowski et al., 2000). The global carbon cycle consisted of the terrestrial and oceanic "biologically active" zones that are connected through gas exchanges with the atmosphere (Siegenthaler and Sarmiento, 1993). However, Sundquist et al. (2009) argue that the natural carbon cycle consists of six significant stores that include: the atmosphere, geological formations and fossil fuels, the oceans, ocean sediments, soils and vegetation. There are also significant fluxes between these carbon stores that include respiration and photosynthesis, weathering and sedimentation, gas exchanges, and transportation by rivers that cycle on timescales from seconds to millennia. The terrestrial biosphere has a fundamental role in the climate system providing both positive and negative feedbacks to climate change and the advent of the industrial age has changed the way carbon is transported between the major carbon stores by disturbing natural fluxes and creating new pathways and potential feedback mechanisms (IPCC, 2007). Figure 1.1 (Sundquist et al., 2009) shows that the estimated release of industrially derived carbon dioxide (CO_2) and to a lesser extent, land-use change have increased the amount of carbon stored in the atmosphere by one third of

pre-industrial estimates (~220 Petagrams[1]; Pg). The increase of atmospheric CO_2 in now of growing concern as it causing significant warming of Earth by changing the heat and water balances between the surface and atmosphere (Sundquist et al., 2009). Consequently, finding ways of reducing the release of carbon from human activity has become of central importance to mitigate possible climate change.

Terrestrial carbon is inter-linked with the hydrological cycle through various chemical and physical processes (Betts et al., 2004a; Betts et al., 2007; Cox et al., 2000; Pielke et al., 1998; Seneviratne et al., 2006). Understanding the relationship between terrestrial carbon and the water cycle is essential to gain a comprehensive understanding of the role that terrestrial ecosystems play in the global climate change (Chen and Coops, 2009).

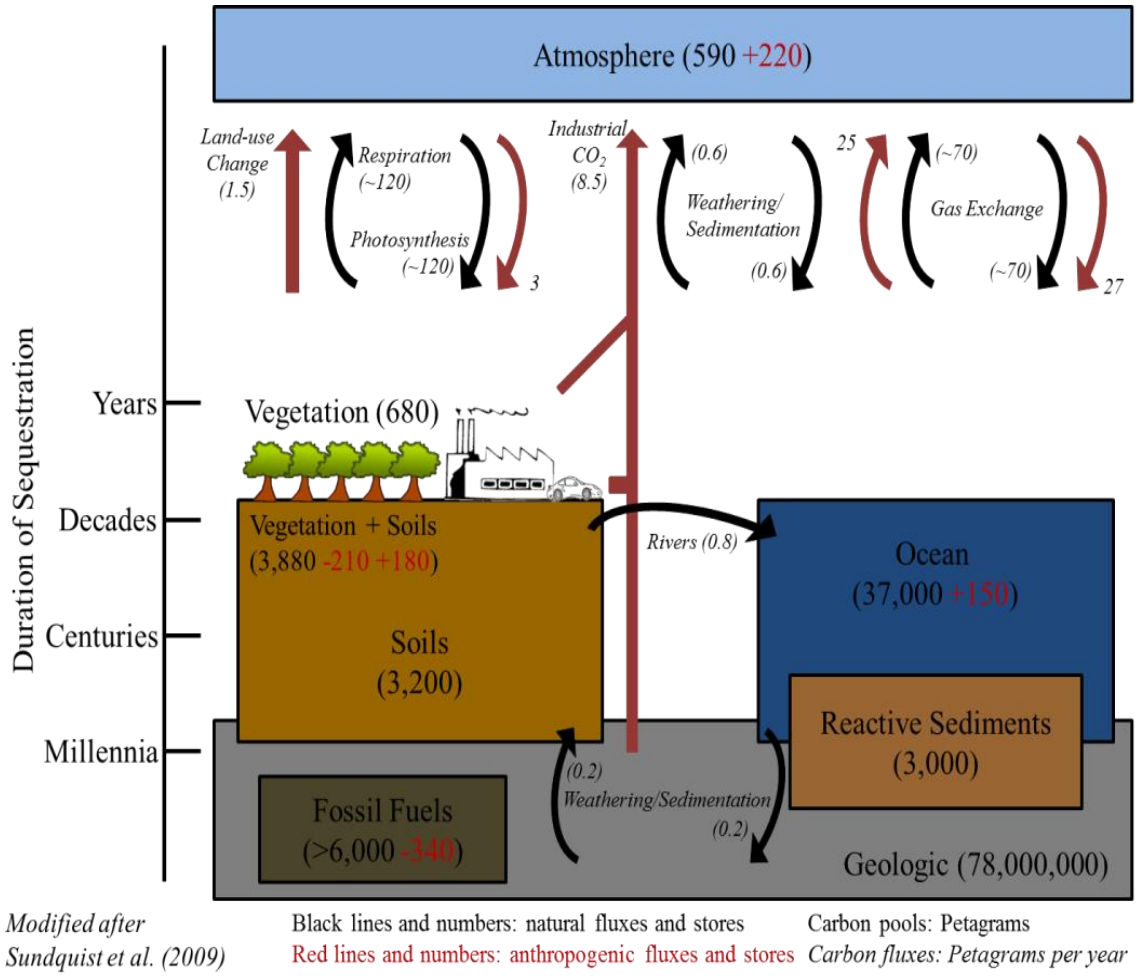

Figure 1.1: The natural carbon cycle and the effect of human activity.

[1] 1 petagram = 1 gigatonne = 10^9 tonnes

Two of the biggest hot spots of the current global carbon cycle are the Arctic and Tropical regions (Wigley and Schimel, 2000) but the scale of hot moments are significantly different due to the variable flux of energy as heat and water availability (McClain et al., 2003). For example, contemporary biogeochemical hot moments in the Arctic are linked to rapid processes such as the erosion of coastal and subsea permafrost (Vonk et al., 2012) and the riverine transport of carbon during the spring freshet (Holmes et al., 2012; Raymond et al., 2007). However, the geological record suggests that Arctic hot moments may have also occurred over much longer timescales with short periods when significant amounts of freshwater and carbon were washed into the oceans. Examples are the 8.2 kyr freshwater event (Alley et al., 1997; Barber et al., 1999), the last glacial termination that occurred ~18,500 years ago and lasted over 4,500 years (Rasmussen et al., 2006; Shen et al., 2005) the Palaeocene/Eocene boundary thermal maximum (PETM), which occurred ~55,000,000 years ago over ~150,000 years (Bowen et al., 2004; Zachos et al., 2003) and the various Oceanic Anoxic Events in the Cretaceous Greenhouse, most of which were at least partly triggered by massive variations in continental runoff (Beckmann et al., 2005; Jenkyns, 2010; Wagner et al.)

In contrast, tropical forest biomes operate on much shorter timescales from inter-annual, seasonal and individual events such as floods and droughts (Marengo et al., 2011a; Marengo et al., 2011b; Tomasella et al., 2011), hurricanes (Yoon and Raymond, 2012) and precipitation events (Johnson et al., 2006a). Paleo-reconstructions of variations in rainforest extent and internal dynamics are scarce and only indirect (Kellman and Tackaberry, 2004), emphasising the extremely fast turnover rates of carbon and water in these unique ecosystems.

1.2 Tropical forests: hotspots of fast carbon and water cycling

Tropical forests are one of the most important biomes on Earth, providing a variety of key resources and ecosystem services, and are estimated to support 50% of all species on the planet (Malhi and Grace, 2000). These forests exchange massive amounts of water, carbon and energy with the atmosphere (Fisher et al., 2009; Foley et al., 2003; Malhi et al., 2009) and have the greatest impact on riverine carbon transport to the ocean (Mayorga et al., 2005; Meybeck, 2006) than any other biome. Tropical ecosystems are threatened by changing climate and land-use (Balch et al., 2008; Brando et al., 2008; Davidson et al., 2008; Lewis et al., 2004; Nepstad et al., 2008) and consequently, there have been increased efforts during the past two decades to understand and predict ecological dynamics in tropical forests at multiple scales

(Townsend et al., 2011). One key focus of research has been to establish the timescales of hot moments where tropical forests cycle water and carbon in its various forms and determine how the interactions of inland water bodies, such as rivers and lakes (hot spots), control the forcing and feedback of carbon and water on a global scale (Aufdenkampe et al., 2011; Bonan, 2008). Battin et al. (2009) demonstrate this concept nicely in the 'boundless carbon cycle' which highlights the current knowledge of carbon fluxes through inland waters aimed at improving the understanding of rivers and the carbon cycle (Figure 1.2).

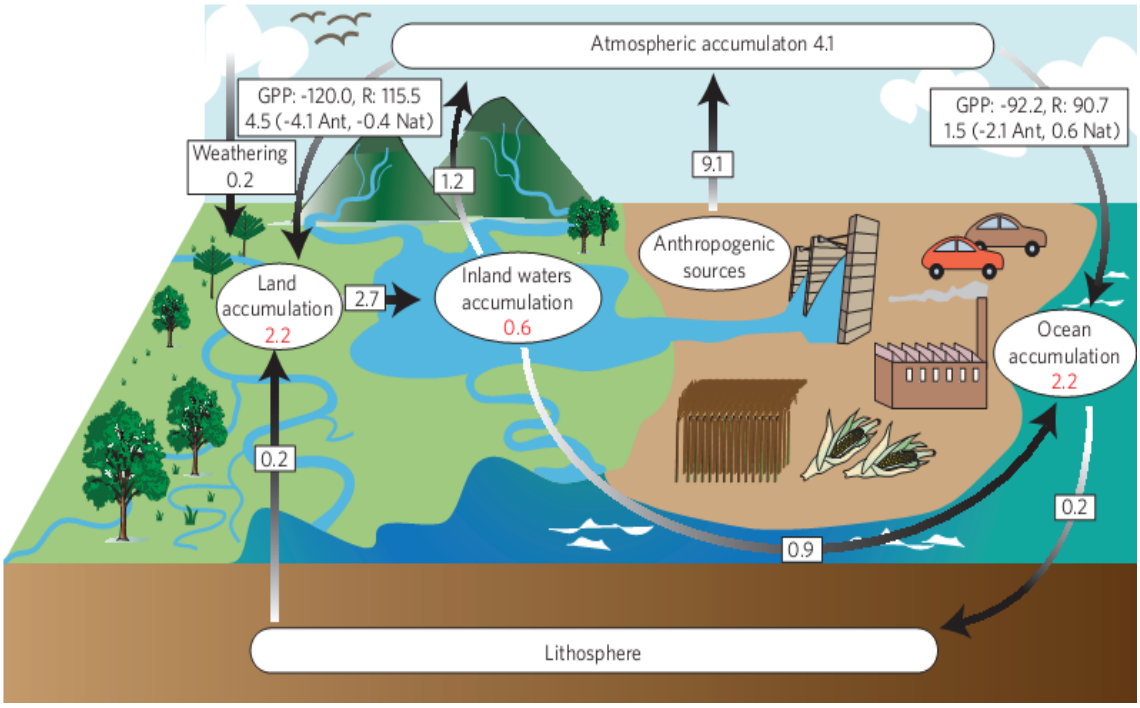

Figure 1.2: The boundless carbon cycle after Battin et al. (2009). Values are net fluxes between pools (black) or rates of change within pools (red); units are Pg of carbon per year; negative signs indicate a sink from the atmosphere. Gross fluxes from the atmosphere to land and oceans, and the natural (Nat) and anthropogenic (Ant) components of net primary production. Fluxes to the lithosphere represent deposition to stable sedimentary basins, and the flux from the lithosphere to land represents erosion of uplifted sedimentary rocks.

The Earth's forests cover approximately 42 million km^2, which is 31% of the global land surface (FAO, 2010). Tropical forests account for 44% of the global forest total and are generally located in the equatorial zone between the tropical latitudes of Cancer at 23° N and Capricorn at 23° S. Tropical forests have two biomes, tropical rainforest which make up about 86% of tropical forest and tropical seasonal forest, accounting for the remaining 14% (Holzman, 2008). Tropical rainforests occur closer to the equator where temperature, rainfall and day length are near consistent throughout the year. In contrast, tropical seasonal rainforest experience notable seasonal changes as they are

located further from the Equator. Tropical rainforests consist of broadleaved evergreen forest and are usually found at elevations below 1000 m and where the temperature is warm year-round and rainfall is high. Average annual temperatures for tropical forests range from 26-27 °C but daily temperature can be more varied, changing up to 4.5 °C due to cloud cover and rainfall (Holzman, 2008). Generally, tropical rainforests receive 2500-4500 mm of rainfall per year but there can be seasonal variations which result in wet and dry seasons (Holzman, 2008); however, in the rainforest the dry season is not truly dry and during this time rain falls intermittently.

1.3 Regional climate and feedback mechanisms of tropical rainforests

Two global systems that affect tropical rainforests are the Inter Tropical Convergence Zone (ITCZ) and the Trade Winds, which are central elements of Hadley Cell circulation. The abundance of heat and moisture in the equatorial zone creates warm air masses that rise into the atmosphere. The rising air causes a low to high pressure gradient from the Equator towards the mid-latitudes which moves warm and humid air away from the Equator and brings cooler and dry air back. This movement generates a general circulation pattern that moves air towards the Equator from the Northern and Southern hemispheres. As these air masses flow and meet at the Equator a zone of unstable air is created, which is called the ITCZ. The ITCZ generally oscillates between 5° N and 5° S of the Equator depending on the amount of solar energy received. The seasonal movement of the ITCZ is generally greater over land and brings significant amounts of rainfall (McGregor and Nieuwolt, 1998). In the absence of the ITCZ the Trade Winds dominate, always blowing from east to west. When the ITCZ is to the north of the Equator the winds are of variable direction and heavy rain is produced while south-easterly winds prevail south of the equator. When the ITCZ is to the south, north-easterly winds prevail north of the ITCZ (McGregor and Nieuwolt, 1998).

Tropical rainforests are an important feedback that recycle water and generate rain over vast distances (Bovolo et al., 2012; Da Silva et al., 2008; Hasler et al., 2009; Wang and Fu, 2007; Werth and Avissar, 2002; Zhang et al., 1996a; Zhang et al., 1996b). Trees return water to the atmosphere through the process of evapotranspiration, which in turn causes of cloud formation above the rainforests. This process releases energy as latent heat which feedbacks into the general circulation of air masses (Osborne et al., 2004). The clouds created by rainforests also reflect incoming sunlight and shade the underlying land thereby reducing surface temperatures (Jackson et al., 2008; Pielke et al., 1998).

1.4 Revising the role of tropical rainforests and rivers in the carbon cycle

Tropical forests account for nearly 40% of terrestrial net primary production (Townsend et al., 2011) and contain approximately 17–25% of the carbon in the terrestrial biosphere (Bonan, 2008) on only ~10% of the land surface (Lewis, 2006). The majority of tropical forest carbon is sequestered in aboveground living biomass (e.g. trees), with secondary stocks in soils and coarse woody debris (Gibbs et al., 2007). Soil carbon, including root material, average about 20% of the total carbon stored in tropical forests (Asner, 2009; Cairns et al., 1997). The sizable carbon pools of tropical ecosystems alone suggest that the tropics have a disproportionate ability to affect atmospheric CO_2 levels in response to changing environmental conditions (Clark, 2007; Luyssaert et al., 2007). Intact tropical forest are thought to be a major CO_2 sink (Lewis et al., 2009; Phillips et al., 2008; Stephens et al., 2007); however, the outgassing of CO_2 of inland tropical waters and wetlands have until recently been missed in the overall budget of carbon sequestration and is likely to make rainforest biomes carbon neutral (Richey et al., 2002).

On a global scale there are major differences in the types of carbon transported to the ocean by tropical rivers. Upland catchments generally export greater amounts of particulate inorganic carbon (i.e. carbon that is greater than 0.45 µm or 0.7 µm and derived from mineral weathering) compared to lowland tropical rivers that are typically located between the latitudes of 3° N and 6° S and have high dissolved organic carbon loads (i.e. carbon that is less than 0.45 µm or 0.7 µm and derived from either living or dead biomass; Huang et al., 2012). The transportation of carbon by rivers as "pipes" to the ocean has historically been recognised as a significant pathway within the global carbon cycle (Meybeck, 1982; Schlunz and Schneider, 2000). However, recently, the paradigm of rivers as "passive pipes" has been challenged as annual global estimates show that 2.9 Pg of carbon enter rivers from the land (Tranvik et al., 2009) but only 0.9 Pg of carbon is delivered to the oceans (Cole et al., 2007). This suggests that rivers are actually "active pipes" that process, store and recycle carbon (Cole et al., 2007). It is therefore critical to know the amount of carbon entering and leaving rivers in various terrestrial ecosystems to accurately estimate global fluxes (Battin et al., 2009). Tropical rivers are estimated to export 0.53 Pg of carbon per year (Huang et al., 2012) and if Amazonian CO_2 evasion rates are representative of the remaining tropics then an estimated ~0.9 Pg of carbon per year is outgassed to the atmosphere by tropical rivers (Richey et al., 2002). However, these estimates need to be verified as relatively few

tropical rivers have been studied with small, low-latitude river systems greatly under-sampled (Eglinton and Repeta, 2003). Where data is available, the focus is usually on the main channel or tidal limit of the big rivers such as the Amazon, Orinoco or Congo (Battin, 1998; Richey et al., 1990). This approach integrates the biological and chemical signatures of the wider catchment over time but at the cost of poorly understanding the changing dynamics between upper headwaters and their larger, downstream counterparts. This is particularly evident in the tropics where a few studies have shown that tropical headwater rivers draining rainforest contain large amounts of dissolved organic carbon (DOC) and are highly saturated in CO_2 compared to downstream rivers (Johnson et al., 2006b; Mayorga et al., 2005; Richey et al., 2002; Spencer et al., 2012; Waterloo et al., 2006). The importance of upper headwater catchments is further emphasised by the observation that second order streams[2] typically account for 70-80% of the total river network (Gomi et al., 2002) and that the terrestrial-aquatic interface is a hot spot of biogeochemical activity (McClain et al., 2003). Consequently, if we wish to manage the carbon cycle on a global scale more studies are required that aim to improve our understanding of riverine carbon fluxes in tropical zones.

1.5 Forest sustainability and carbon management

Tropical forests are much more than just carbon and water cyclers. They sustain biodiversity; provide habitats and homes to indigenous people, a multitude of natural products such as food, building materials and medicines, and a number of ecosystem services including soil stabilisation and flood prevention (Batistella et al., 2009a). The rates of carbon sequestration of tropical biomes are complicated by human interactions. For example, the annual deforestation of tropical forest alone is estimated at 476,000 km^2 (Hansen et al., 2010)), which is expected to release 2.9 Pg of carbon into the atmosphere. This is equivalent to a third of present day global carbon emissions (Pan et al., 2011). Conversely, forest regeneration in tropical areas is removing 1.6 Pg of carbon from the atmosphere, which partially offsets the emissions from deforestation (Pan et al., 2011). Although difficult to accurately quantify, tropical deforestation and related land-use changes are likely to account for a substantial fraction of anthropogenic CO_2 emissions each year (Ramankutty et al., 2007; Townsend et al., 2011). To address this issue, international proposals have gained momentum to compensate developing

[2] The Strahler ordering system defines the stream size based on a hierarchy of tributaries where the smallest river is categorised as 1. When two number 1 tributaries meet the resulting stream in classified as 2. Where two 2's meet a 3 is defined and so on…

countries that succeed in reducing emissions from deforestation (RED) with financial incentives (Ebeling and Yasue, 2008); tradable carbon credits alone could potentially generate US$2.2-13.5bn if deforestation rates were reduced by 10% of current levels (Ebeling and Yasue, 2008; Laurance, 2007). Identifying responses to forest change is a key component of the reducing emissions from deforestation and forest degradation (REDD+) programme of the United Nations Framework Convention on Climate Change (UNFCCC). It defines five sets of activities or interventions, namely; reducing emissions from deforestation, reducing emissions from forest degradation, conservation of (existing) forest carbon stocks, sustainable management of forests, and enhancement of forest carbon stocks (Gardner et al., 2012). Reduced impact logging (RIL) practices aim to minimise the disturbance of tropical forest carbon and water cycles via pre-harvest tree selection and vine cutting, directional felling, and planned extraction (skid) trails and log decks (Miller et al., 2011; Pinard and Putz, 1996; Uhl et al., 1997). RIL has been shown to reduce canopy destruction and minimalize forest alteration (Pereira et al., 2002; Pinard and Putz, 1996). However, forest degradation from RIL and in particular, changes in forest carbon stocks and the underlying mechanisms are more difficult to ascertain (DeFries et al., 2007).

1.6 Current challenges in global carbon cycling and implication for the tropics

Interdisciplinary science that integrates the knowledge of carbon and water cycles of tropical forest biomes are essential to better characterise feedbacks in the Earth system and understand the potential of forests to mitigate climate change (Bonan, 2008). Given the hot moments of carbon at the terrestrial-aquatic interface (McClain et al., 2003; Richey et al., 2002) and the current lack of data available from tropical headwater rivers, it is critical to ascertain the amount of carbon and its composition entering the river to accurately estimate global fluxes (Battin et al., 2009). However, this is not an easy task as measuring the flux of carbon between the land and river is complicated by the interaction of carbon and hydrology cycles, the temporal and spatial variability of these cycles, the compositional variability of carbon and our technical capability to accurately identify and quantify the key components (Aufdenkampe et al., 2011; Cole et al., 2007; Eglinton and Repeta, 2003).

These challenges highlight the motivation of this project:

Carbon composition, interactions and analytical capability: The large variability of carbon structures in the natural environment is daunting. The ability to detect responses

to climate and land use change in rainforest systems is therefore very challenging (Townsend et al., 2011; Wohl et al., 2012). The complexity of a multitude of biogeochemical interactions with carbon (e.g. N, P, K and water) also causes large variability of ecosystem functionality (Townsend et al., 2008) and the potential for multiple limiting nutrients (Vitousek et al., 2002; Vitousek et al., 2010; Vitousek and Sanford, 1986) that will ultimately control carbon sequestration (Townsend et al., 2011). Whilst bulk measurements of carbon are relatively robust at providing assessments of carbon quantity they give little information on the mechanisms of formation, transport and storage. No single set of tools are adequate to address the variety of carbon compositions in the environment and so a variety of different analytical approaches are required. Fractionation and chromatographic techniques have all been used to derive useful information on the relative contribution of different pools of carbon (e.g. thermally labile vs. recalcitrant (Manning et al., 2005)) and isolate individual organic compounds, known as biomarkers, that are indicative of a particular organism or process (e.g. archaeol as an indicator for methanogenesis (Lim et al., 2012)). Isotopic/radiocarbon information also provides valuable evidence on the age that carbon was preserved and from which environment. However, interpretation of biomarkers and isotopic data is not straightforward as they only provide highly specific information and do not tell the whole carbon story. To address this weakness, it is necessary to combine detailed molecular organic geochemistry with compound class-specific and bulk analysis.

Temporal variability: Recent changes in patterns of precipitation and temperature in the tropics, most notably in Amazonia have demonstrated that there is an increasing trend in unpredictable events such as floods and drought (Lewis et al., 2011; Marengo, 2009; Marengo et al., 2011b). These events have shown that Amazonian trees are somewhat resilient to water stress during drought but it is unclear to what extent forest carbon cycles are affected (Saleska et al., 2003). The rate at which carbon is cycled (known as carbon turnover) in tropical environments is equally challenging to ascertain. An extensive survey of Amazonian rivers found that bulk organic carbon pools had different ages with the dissolved fraction displaying younger ages than the particulate fractions (Mayorga et al., 2005). Superimposed on this, carbon outgassed as CO_2 was observed to be less than five years old; suggesting a rapidly recycled pool of organic carbon is responsible for a significant carbon flux to the atmosphere via the terrestrial-aquatic boundary (Mayorga et al., 2005). Davidson et al. (2010) demonstrated that

groundwater sources are not significantly contributing to riverine CO_2 outgassing. Therefore, whether the major pathway of riverine CO_2 outgassing is a result of CO_2 transported across the terrestrial-aquatic boundary (Mayorga et al., 2005) or DOC that is mineralised within the water column (Richey et al., 2002) is still an open but critical question.

Spatial variability: On a global scale there is a substantial uncertainty in hydrological trends on a global scale because of large regional differences, gaps in spatial coverage and temporal limitations in the data (Huntington, 2006). For example, available stream flow gauge records cover only about two- thirds of the global actively drained land areas and they often have gaps and vary in record length (Dai and Trenberth, 2002). With regard to carbon, there are significant discrepancies in estimates of carbon fluxes from different regions depending on whether a top-down or bottom up approach is used. This is mainly because the coarse spatial resolution of inverse models cannot capture variations between distinct changes in land type (Janssens et al., 2003; Pacala et al., 2001). Likewise, the large heterogeneity within ecosystems makes up scaling data from the micro-scale to local-scale and then to the wider region extremely challenging (Battin et al., 2009).

1.7 Research questions, objectives and hypotheses

One of the overarching research questions for tropical rainforest management is how to respond to combined naturally and anthropogenically induced change. To address this broader question, a sound science baseline characterising the state of the forest within the current variability of dry and wet seasons needs to be established. This baseline will provide the basis and evidence to identify and quantify the response to external forcing including quantity and composition of the carbon cycled in soil and water. The aim is to characterize and quantify the hot spots and hot moments of tropical rainforest headwaters within the seasonal climate context. This motivation leads to the main objective to establish the range of hydrological variability and its effect on the leaching of carbon from soils and its subsequent transport and alteration in headwaters. The focus is on the partitioning of carbon between low and high molecular weight pools of organic matter, within the seasonal climate cycle, between pristine and anthropogenically influenced areas in the forest, and in response to precipitation events.

The hypotheses to be tested are:

i. *The amount of organic carbon exported from riparian soils to the river in tropical headwaters catchment is linearly related to rainfall approaching peak levels during precipitation events and exhibits a dry to wet seasonal pattern.*
ii. *Organic carbon is distributed in two main pools of organic matter: (1) low molecular weight and labile and (2) higher molecular weight and more refractory. A large fraction of the high molecular weight, older OM is remineralised while travelling through headwater catchments, resulting in preferential export of low molecular OM to the larger river system.*
iii. *The anthropogenic influence on the carbon cycling is amplified in reduced impact logging (RIL) areas when compared to pristine conditions, and detectable with the proposed sampling and analytical approach.*

1.8 Thesis layout

This thesis is based on three manuscripts that are either in preparation, submitted or under revision. The study area and the methods used to investigate whether tropical lowland rainforests are rapid recyclers or efficient sinks of carbon are in chapter 2. Chapter 3 compares newly recorded rainfall data from central Guyana against two global tools that are widely used to infer local climate. Chapter 4 looks at the timescales involved of the storage and mobilisation of carbon from a paired catchments experiment in two small-scale headwaters. Chapter 5 highlights the rapid mobilisation of carbon by rivers during a rainfall event in the wet season and identifies labile carbon groups that may provide a source of carbon for riverine CO_2 outgassing. Chapter 6 syntheses the core research findings and discusses the research agenda for future tropical work.

Chapter 2: Materials and Methods

2.1 Approach

This study aims to characterise and quantify the export signal of organic carbon and nutrients from the smallest hydrological unit of tropical forest headwater catchments, and assess the dynamic response to seasonal climate variations (dry and wet) and local impact from reduced timber forestry activity. One of the overarching research questions for tropical rainforest management, targeted at Iwokrama in central Guyana, is how to respond to combined natural and anthropogenic induced change. To address this broader issue, a sound science baseline characterising the state of the forest within the current seasonal variability of dry and wet seasons needs to be established. This baseline provides the evidence to identify the response to external forcing including quality and cycling of carbon in soil, water and river bed sediments at the catchment scale.

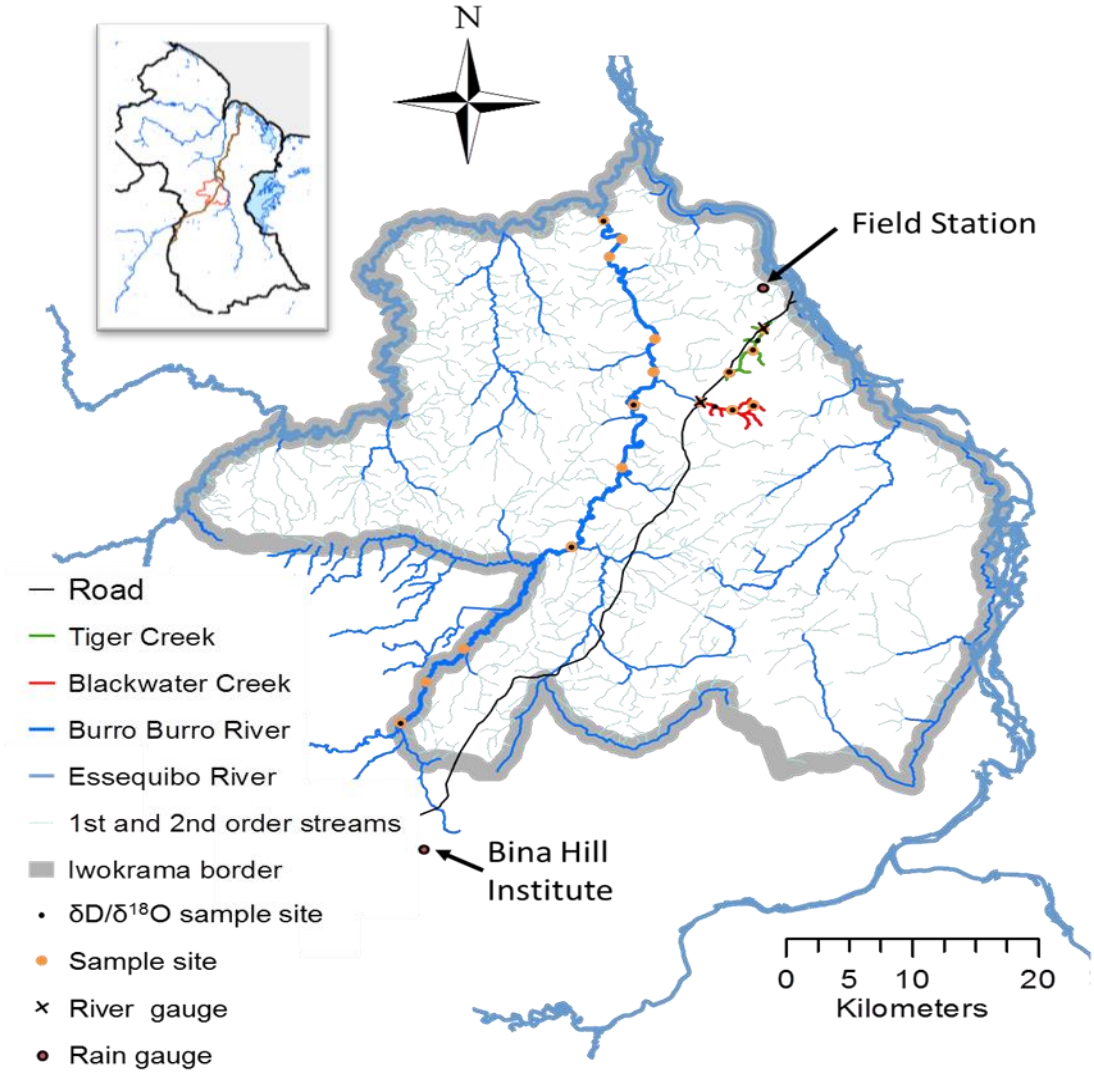

Figure 2.1: Iwokrama and relevant tributaries of the Burro Burro catchment, focus catchments with new instrumentation sites and sample locations.

2.2 Study area

The Iwokrama reserve comprises of 3710 km^2 of rainforest in central Guyana (Figure 2.1) bounded by the Essequibo River to the East and the Siparuni River - a tributary of the Essequibo catchment - to the west and north (Figure 2.1) and lies just north of the Rupununi savannah grasslands in the south. Iwokrama is situated near the northern extent of the ITCZ, where there is a transition in the climate regime from north (coastal) to south (savannah) of two wet seasons (primary: May-July and secondary: December-January) and two dry seasons (primary: September-November and secondary: February-April) to one wet season (May-August) and one long dry season (September-March; Bovolo et al., 2012).

The Burro Burro catchment, a tributary of the Essequibo River, which drains the 10^{th} largest river catchment in South America (Dai and Trenberth, 2002), covers some 3200 km^2 with approximately 2020 km^2 situated within the Iwokrama Reserve (Hawkes and Wall, 1993). The main channel of the Burro Burro River dissects the Iwokrama forest south to north from the southern boundary of the forest-savannah transition, forming an approximate 65 km riverine transect. The underlying geology consists of acid-intermediate volcanics intermixed with granitoids and dolomites, which is predominantly overlain by highly leached, white and brown quartz sands (Hawkes and Wall, 1993).

Within the Iwokrama reserve, two small, lowland headwater catchments were studied; Blackwater Creek (BWC) is slightly larger at ~20 km^2 and ~6 km long compared to Tiger Creek (TC) which covers ~17 km^2 and is ~5 km long. These 'focus' catchments are located within 1.5 km of each other and discharge into the Burro Burro River (Blackwater Creek); and directly into the Essequibo River (Tiger Creek). Both focus catchments are situated on similar acid-intermediate volcanic geology, overlain with highly-leached, quartzite, brown and white sands. They are both dominated by ferralsol soils (under the FAO, 1998 classification system by Deckers et al. (1998)), which is the most common soil of Central Guyana (van Kekem, 1996). The A horizon (0.0 to 0.1 m) is characterised by a typically major sand fraction with high amounts of silt/clay and rootlet material. The underlying sub-soil (0.1 to 1.0 m) is comprised of two sand layers with a minor fraction of silty material adding a brownish colour from 0.1 to 0.4-0.6 m compared to deeper sands (0.4-0.6 to 1.0 m), which are white and saturated, consistent with the Kurupukari sand terraces geological description of central Guyana (Hawkes and Wall, 1993).

Blackwater and Tiger catchments contain similar forest types dominated by greenheart (*Chlorocardium rodiei*), black kakaralli (*Eschweilera subglandulosa*) and wamara (*Swartzia leiocalycina*). However, one notable difference between the catchments is that the Tiger Creek catchment was harvested for commercial timber species from 2007 to 2009 using reduced impact-logging (RIL) techniques, removing approximately 12.5 m^3 of biomass per hectare per 60 year cutting cycle. In total 401 trees were removed from 2007-2009. When compared to conventional clear-fell logging techniques, the impact of RIL upon a forest ecosystem is significantly mitigated by reducing the number of trees damaged during logging and aiding ecosystem recovery rates (Macpherson et al., 2012; Miller et al., 2011; Pinard and Putz, 1996).

2.2.1 *Installation*

The new hydro-climate and geochemistry-monitoring programme installed in March 2010 combines an automatic weather station (AWS; Casella CEL, Bedford, United Kingdom)) with river gauges within the Iwokrama forest. This complements a pre-existing manual storage rain gauge (127 mm diameter) in the savannah lands of Annai to form a north-south meteorological transect monitoring the precipitation patterns across a strong change in forest and savannah biomes (Figure 2.1). Prior to March 2010, total daily rainfall was recorded at Iwokrama Field Station using a standard manual storage rain gauge (127 mm diameter). Where daily rainfall was not recorded (either manually or by the AWS) totals were approximated using accumulated measurements from the storage rain gauge. The two focus catchments were instrumented for stage using DCL 9500 Level Sensors (Gems) calibrated to manual stage board readings. The sensors were housed within a stilling well and connected through a vented cable to a Frog RX data Logger (Isodaq Technology). Flows were measured periodically across the range of observed conditions using a StreamPRO ADCP (Acoustic Doppler Current Profiler; Teledyne RD Instruments) at Blackwater Creek, and a Braystoke current meter (Valeport) at Tiger Creek. Rating curves were constructed using these data, and used to convert the monitored stage into flow records for each focus catchment.

2.2.2 *Sampling*

Burro Burro Catchment

To complement the hydro-climate monitoring programme, river water samples were collected from the main channel of the Burro Burro catchment during the dry and wet seasons (March and July) of 2010 (Figure 2.1). In total, 24 locations were sampled at

approximately 0.5 m depth from a boat and 48 water samples were collected during 2010. All samples were filtered (0.45 µm Pall SUPOR Acrodisc) in the field and then kept frozen in Nalgene bottles in the dark.

Focus Catchments

From Blackwater (control) and Tiger (managed) catchments, river water, river bed surface sediments and riparian soils were collected from three sampling stations approximately 1.5 kms apart. Sample stations were located from the source of the focal catchment to the exit (defined by the location of the river gauge described in section 1.2). Each sample station was sampled during the dry and wet seasons of 2010 and again in 2011 (March and June/July in each year). In July 2010, soil samples were also collected at 0.5m and 1.0m below ground level (bgl). Sampling dates were: Blackwater Creek on 05/03/2010, 29/07/2010, 25/03/2011, 23/06/2011; Tiger Creek on 03/03/2010, 17/07/2010, 26/03/2011, 22/06/2011; and Burro Burro River on 20-22/03/2010, 10-12/07/2011.

In total, 12 river water, 12 river bed sediment and 21 soil samples were collected from each focus catchment during the project lifespan. All water samples were field filtered using Pall Acrodisc 0.45 µm SUPOR filters (Karanfil et al., 2003) and stored frozen in Nalgene bottles. All soils and sediments were stored frozen in pre-cleaned amber glass jars.

To ascertain the role of rain events in riverine DOC transport, river water samples from Blackwater Creek were collected from the main channel at the same location as the river instrumentation (section 2.2.1). In total, 24 samples were collected over 13.5 hours on the 7th July 2011. All samples were filtered (0.45 µm Pall Acrodisc) in the field and then kept frozen in Nalgene bottles in the dark.

2.3 Sample Analysis

2.3.1 *Bulk Soil Carbon and Nitrogen*

All soils and river bed sediments were freeze-dried and ground to pass a <200 µm sieve. Organic carbon content (TOC) was determined by removing carbonate with 0.5 M HCl and analysed by LECO CS 244 Carbon-Sulphur -elemental analyser according to the method by (Krom and Berner, 1983) at Newcastle University. Selected samples were run in triplicate and the mean value reported with the standard error better than 0.055%. Total carbon (TC) and nitrogen (N) were determined using a VarioMax (Elementar

Analysensysteme, Germany). All samples were analysed twice with the mean value reported. The standard error was less than 0.014% where an analytical detection limit is applied at 0.01% dry weight (% dwt). Comparison of TC and TOC results show that soils and river bed sediments are predominately comprised of organic carbon with little variation between reported values (C: +/- < 0.24% dwt). This range is within the standard error of analysis of both methods plus the range reported for the standard reference material used (C: +/- 0.18% dwt). Water samples were analysed at Newcastle University for organic carbon using high temperature catalytic oxidation on a Shimadzu-5050A TOC analyser with an ASI-5000A auto-sampler; all samples were analysed in triplicate and the mean value used. The standard error was better than 0.65 mg/L.

2.3.2 *Chromophoric dissolved organic matter*

Chromophoric dissolved organic matter was determined using the spectral absorbance of river water. UV absorbance was measured from 200-800 nm in a field laboratory using a WPA II Lightwave UV-Vis spectrophotometer (Biochrom). Samples were measured using a 10 mm quartz cuvette blank corrected using a sealed quartz cuvette containing high purity water (PerkinElmer). Replicate measurements were made on selected samples with the relative standard deviation never more than 0.5%.

2.3.3 *Carbon fractionation*

Dissolved organic matter composition was determined at the Helmholtz Centre Potsdam using size-exclusion chromatography (SEC), which separates the DOM pool into different size fractions based on compound group retention behaviour, reference materials and standards, as well as the amount of organic carbon compared to UV absorbance reactivity (Huber et al., 2011). The setup uses a novel organic carbon detector and UV absorbance detector at 254 nm Huber et al. (2011) and follows the method by Sachse et al. (2001). Briefly, a HW-50S column (250 mm x 20 mm inner diameter, Toyopearl) and phosphate buffer eluent (0.029 M, pH 6.5) at a flow rate of 1 mL/min were used to separate five different DOC groups (humic substances, calibrated to Suwannee River “IHSS-FA and IHSS-HA” standard and building blocks, considered breakdown products of humics, grouped together as “humics”; low molecular weight neutrals referred to as “iDOM”; low molecular weight acids, and biopolymers (typically polysaccharides, amino sugars, polypeptides, proteins) referred to as “other”; Figure 2.2). At the effluent of the column, DOC fractions are characterized by UV-detection

(254 nm) and quantified by IR-detection after UV oxidation in a cylindrical UV thin-film reactor (Gräntzel, Germany; 185 nm; Figure 2.2). Replicate measurements were made on selected samples with the standard error never more than 6%.

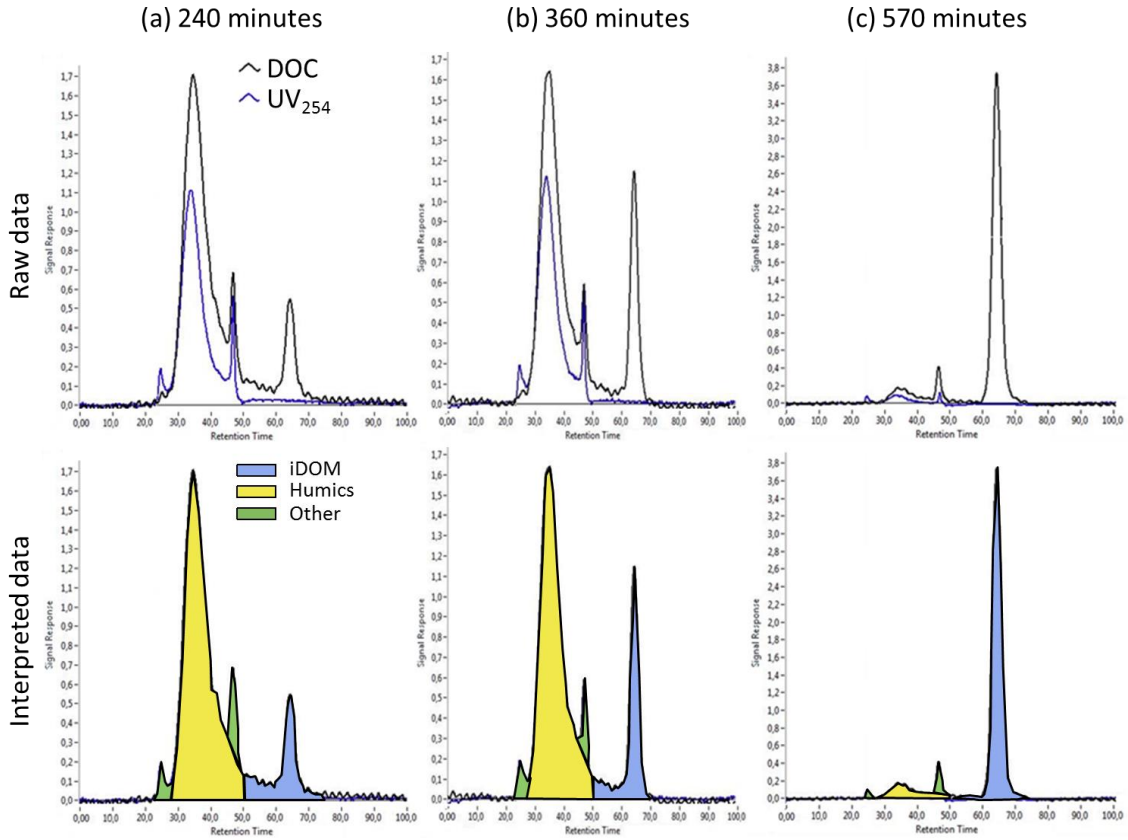

Figure 2.2: SEC chromatograms of samples at 240, 360 and 570 minutes. Data shown as raw chromatograms with IR- and UV-detector response and interpreted groups of humics, iDOM and other compounds.

2.3.4 *Aqueous Lignin Sample Preparation*

Whole water samples were acidified to pH 2 with 12 N HCl to minimise precipitation. In order to minimise transfer losses samples were reduced in volume by transferring ~3 mls of sample into Monel reaction vessels (Prime Focus, Inc.) used for CuO oxidation and dried under vacuum centrifugation. The vessel was then refilled with aqueous sample and dried again. This was repeated until 100-175 mls of sample (volume dependant on DOC concentration) had been transferred into the Monel reaction vessel.

2.3.5 *Soil Leachate Experiments*

Soil leachate experiments were conducted on 5 soil samples collected in July 2010. Approximately 2 g of soil was mixed with 10 mL of ultrapure water, shaken for 24

hours and put through a pre-combusted 0.7 µm GF/F filter. A subsample of the filtrate was taken for DOC analysis with the rest of the filtrate sample prepared for lignin analysis.

Table 2.1: Modification of lignin phenol CuO oxidation methodology from Hedges and Ertel (1982) method as summarised by Spencer et al. (2010a).

Original technique (Hedges and Ertel, 1982)	Modification	Reference for modification	Notes
N/A	Addition of glucose to reaction vessel	(Louchouarn et al., 2000)	Minimizes superoxidation effects in low-carbon samples
Overnight purging of samples and reagents in glove box	Direct sparging of reagent bottles (10 min) and purging of reaction vessels in purge block	(Eckard et al., 2007; Louchouarn et al., 2000)	Faster, simpler technique with no measurable difference
14C p-hydroxyacetophenone internal standard with ethyl vanillin as external standard	Ethyl vanillin as internal standard	(Opsahl and Benner, 1995)	Eliminates steps, eliminates radioactive and carcinogenic reagents with no measurable difference
Ethyl vanillin as quantification standard	Cinnamic acid as quantification (internal) standard	(Hernes and Benner, 2002; Opsahl et al., 1999)	Significant ethyl vanillin can be lost during laboratory processing in samples with limited matrix
Oxidation at 170 °C (external reaction vessel temperature)	Oxidation at 155 °C (internal reaction vessel temperature)	(Goni and Hedges, 1992)	More accurate and representative temperature control
Ethyl ether extraction	Ethyl acetate extraction	(Goni and Montgomery, 2000)	Substitutes highly explosive reagent for safer reagent, eliminates distillation step, slightly higher extraction efficiency of syringyl phenols
GC with flame ionization detector	GC with MSD	(Opsahl and Benner, 1997)	Increased sensitivity and eliminates co-elution problems
N/A	Five-point calibration curve with matching internal standard concentrations in all sample and calibration vials	(Hernes and Benner, 2002)	Eliminates non-linearity issues with changing internal standard concentrations
N/A	Quantification by interpolation between two calibration curves	(Spencer et al., 2010a)	Minimizes quantification error associated with changing column characteristics as subsequent samples “dirty” front end of column

2.3.6 *Lignin Oxidation*

Lignin analyses were carried out by CuO oxidation after Spencer et al. (2010a), which is modified from the original method of Hedges and Ertel (1982) and summarised in Table 2.1. Following oxidation in 8% NaOH at 155°C for three hours in the presence of a stoichiometric excess of CuO and glucose (to minimise superoxidation effects), samples were acidified and extracted three times with ethyl acetate and dried using Na_2SO_4 columns. Excess solvent was blown off under a stream of ultrapure nitrogen. Samples were then stored frozen until analysis.

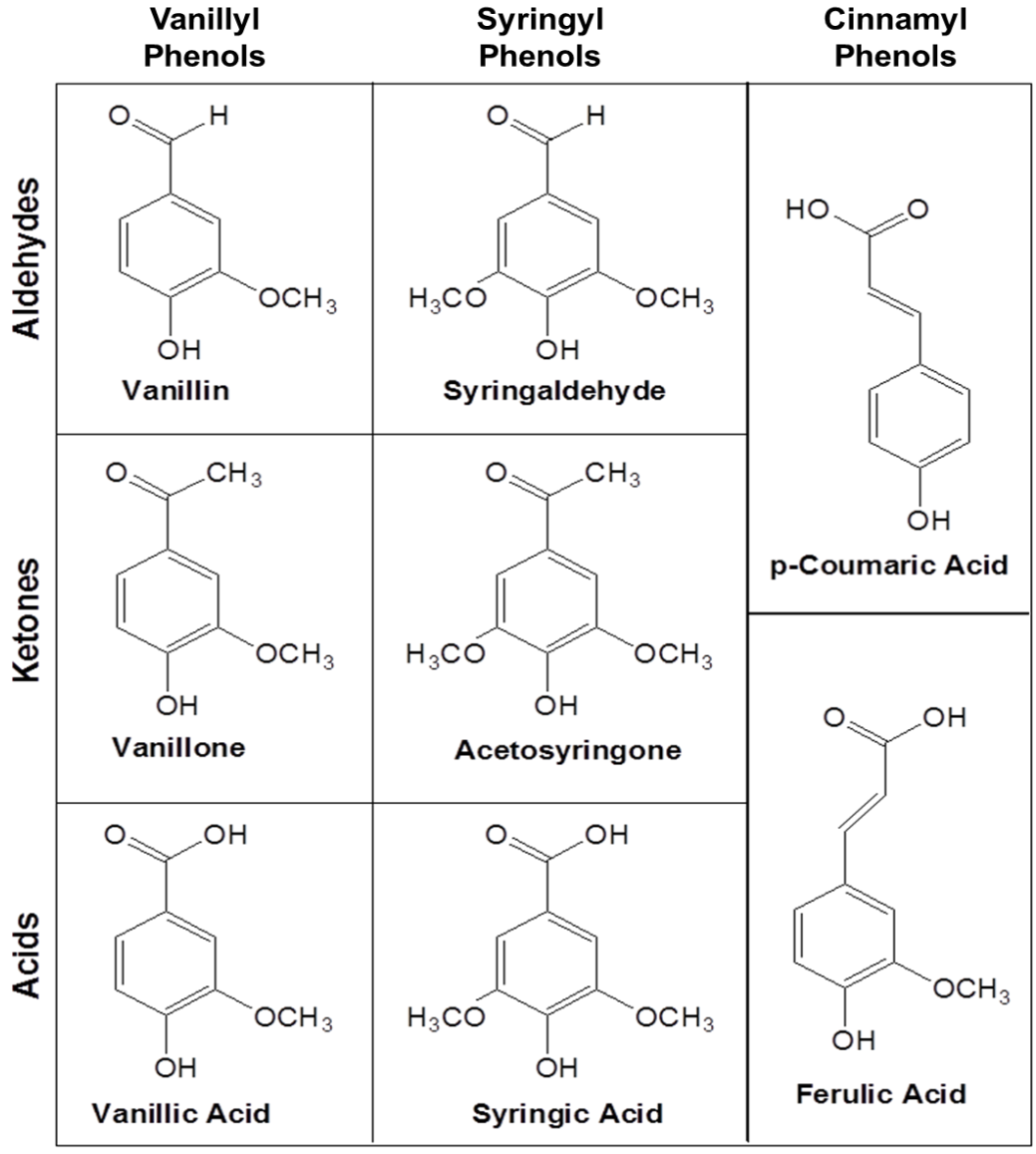

Figure 2.3: Lignin biomarker compounds quantified after CuO oxidation.

Lignin phenols were derivatised using bis-trimethylsilyltrifluoromethylacetamide (BSTFA) and separated using an Agilent 6890 gas chromatograph (GC) fitted with a DB5-MS capillary column (30 m, 0.25 mm inner diameter, J&W Scientific).

Quantification was achieved using an Agilent 5973 mass selective detector interfaced with the GC using selected ion monitoring with cinnamic acid as an internal standard following the five-point calibration scheme of Hernes and Benner (2002). Eight lignin phenols were quantified (Figure 2.3) including three vanillyl phenols (vanillin, acetovanillone and vanillic acid), three syringyl phenols (syringaldehyde, acetosyringone and syringic acid) and two cinnamyl phenols (*p*-coumaric acid and ferulic acid). Blank concentrations of lignin phenols were low (~50 ng total) for the eight lignin phenols measured in this study with total blanks for all eight compounds never <2% of sample measurements. Replicate analyses on seven samples demonstrated that the standard error of analysis was less than 0.046 mg/100 mg OC.

2.3.7 *Stable Water Isotopes*

Water samples were analysed for oxygen and hydrogen isotopes ($\delta^2H/\delta^{18}O$). Oxygen and hydrogen isotopes were measured using a Picarro Cavity Ring-Down Spectroscopy (CRDS) analyser in the School of Chemistry and Pharmacy at the University of East Anglia, Norwich, UK. Three calibration standards, USGS W64444, GISP, and USGS W67400, were run at the beginning and at the end of each sequence of samples. Sample results were calibrated to these standards using linear least squares regression. A laboratory standard NTW (Norwich Tap Water) was measured along with the standards to monitor reproducibility of the results. Each sample was measured 6 times and the first three measurements discarded to account for memory effect. The precision of sample δ^2H and $\delta^{18}O$ measurements was better than 1.2 and 0.3‰, respectively.

2.3.8 *Stable Carbon Isotopes*

Stable isotopic measurements ($\delta^{13}C$) of all soils, river bed sediments and waters were conducted at the Stable Isotope Facility at University California Davis, USA. Soils and river bed sediments were acid fumigated for 6-8 hours in silver foil capsules using a desiccator and 12 M HCl (Harris et al., 2001). Samples were analysed using an Elementar Vario EL Cube (Elementar Analysensysteme, Germany) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Samples are combusted at 1000 °C in a reactor packed with copper oxide and lead chromate. Following combustion, oxides are removed in a reduction reactor (reduced copper at 650 °C). The helium carrier then flows through a water trap (magnesium perchlorate) with N_2 and CO_2 separated using a molecular sieve before entering the isotope ratio mass spectrometer (http://stableisotopefacility.ucdavis.edu/13cand15n.html). Waters

were analysed using an O.I. Analytical Model 1030 TOC Analyser (OI Analytical, College Station, TX) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) with a GD-100 Gas Trap Interface (Graden Instruments). Samples are acidified and purged with helium off-line to remove all dissolved inorganic carbon. An aliquot of sample is transferred into a heated digestion vessel and reacted with sodium persulfate to convert DOC into CO_2 for measurement on an IRMS under helium flow. Results are reported relative to V-PDB (Vienna PeeDee Belemnite) standard. During analysis, samples are interspersed with several replicates of at least two different laboratory standards (IAEA-N1, IAEA-N2, IAEA-N3, USGS-40, and USGS-41) with the long term standard deviation better than 0.4 per mil (http://stableisotopefacility.ucdavis.edu/doc.html).

2.3.9 ***Radiocarbon***

Selected soil, river bed sediment, and water samples from the 2010 field campaign were analysed for radiocarbon ($\Delta^{14}C$) at the NERC Radiocarbon facility in East Kilbride. Prior to analysis by accelerator mass spectrometry (AMS), soil samples were soaked overnight in 0.5 M HCl at room temperature, pH verified to <7, rinsed free of mineral acid with deionised water, dried and homogenised. The total carbon in a known weight of the pre-treated sample was recovered as CO_2 by heating with CuO in a sealed quartz tube. Water samples were acidified to pH 4 by drop-wise addition of 2 M HCl, sparged with nitrogen gas for 20 minutes and pH adjusted to pH 7 with 1 M KOH solution. A measured volume of sample was rotary evaporated in acid-washed glassware, until a few ml of solution remained and quantitatively transferred to an acid-washed glass beaker for freeze drying. The total carbon in a known weight of the pre-treated sample was recovered as CO_2 following combustion in an elemental analyser. All gas samples were then graphitised by Fe/Zn reduction. All samples are reported as Absolute % Modern (Stuiver and Polach, 1977) and conventional radiocarbon age (Years BP) where appropriate. The standard error of replicate analysis is better than 0.53%.

Chapter 3: Validation of rainfall and river isotopic chemistry data from global models with local observations (2009-2011) in northern Amazonia (Guyana)

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Abstract

We use first field-based observations of precipitation and river isotopic chemistry from a three-year study (2009-2011) in rainforest and nearby savannah in central Guyana at the northern rim of the Amazon rainforest to establish the quality of modelled or remotely-sensed datasets. Once the dataset quality and characteristics are established, these can be used as proxies for observations as a first step in characterising the hydrological regime of the area. Our 3 years of data capture a reduced rainfall regime in 2009 and an extended wet season in 2010, in contrast to the widely documented Amazonian floods in 2009 and droughts in 2010. Comparisons of observed precipitation with satellite derived TRMM and ECMWF ERA-Interim reanalysis precipitation show that both of these data sets capture the general pattern of seasonality, but substantially underestimate rainfall amounts in the primary wet season (by up to 50% and 72% respectively). The TRMM dataset is generally better at characterising the main dry season from September to December but the ERA-Interim model can overestimate precipitation in the dry season by up to 175%. Our first data on isotopic chemistry of river waters for the area show that $\delta^2H/\delta^{18}O$ values in this region are broadly consistent with the interpolated global datasets of modelled precipitation isotopic signatures by Bowen et al. (2005). The data further show that during the peak wet season, river water is dominated by rapid runoff from isotopically lighter water derived from the rains of the ITCZ. These results provide evidence of the close coupling of water chemistry of headwater rivers on the northern rim of Amazonia to the positioning of the ITCZ over the region. However, there are significant uncertainties in rainfall quantities in the TRMM and ERA-Interim datasets that need to be addressed within these models, and that should be recognised and allowed for in any future studies in this region.

3.1 Introduction

Amazonian tropical rainforests are important ecosystems for cycling water at local, regional and global scales (Eltahir and Bras, 1994). A number of studies have emphasised the increasing trend of extreme seasonal and inter-annual variability of precipitation and hydrology in the region, such as the severe floods and droughts in 2009-2010 in Amazonia (Lewis et al., 2011; Marengo et al., 2011b; Tomasella et al., 2011), which were attributed to warming of the tropical North Atlantic (Booth et al., 2012) and subsequent anomalous southerly migration of the Inter Tropical Convergence Zone (ITCZ) (Marengo et al., 2012; Marengo et al., 2011b). The associated large variations in fluxes of water released from tropical rivers have been demonstrated, e.g. for the Amazon (Mayorga et al., 2005; Richey et al., 1990; Tomasella et al., 2011) and Orinoco (Battin, 1998; Yamashita et al., 2010) rivers. Significant uncertainties remain in understanding climate dynamics and variability in Amazonia. This lack of knowledge is mainly because of the uneven coverage of field study sites, which do not provide an adequate representation of larger areas (Batistella et al., 2009b). Logistical and other constraints in remote tropical rainforests commonly result in localized, widely scattered datasets, requiring interpolation or up-scaling to understand regional patterns, often based on few ground-based datasets.

In comparison with the central Amazon rainforest, the climate and hydrology of the northern Amazonia rainforests of the Guiana Shield region (incorporating Guyana, Suriname, and French Guiana, collectively known as 'the Guianas', with parts of southern Venezuela and northern Brazil) are even less well known. This region however, has one of the lowest deforestation rates, and incorporates approximately 15% of the forest in South America (Hammond, 2005). As deforestation trends continue elsewhere, the Guiana Shield will increasingly represent a greater share of the remaining intact forest cover (Hammond, 2005), and may provide a crucial link in maintaining moisture transfer from the Caribbean into central Amazonia (Marengo, 2009). There is also uncertainty in the regional climate understanding, reflected by lack of consensus in Global Climate Model future scenarios for the equatorial South American region, and in the Guiana Shield region in particular (e.g. McSweeney et al., 2010), emphasising the need for more small-scale studies that link local processes with larger climate dynamics.

Observation based interpolated climate datasets of the region do not allow an accurate representation of the climate of this area, because they incorporate few, if any records from Guyana (e.g. NOAA Climate Prediction Centre unified gauge-based analysis of

global daily precipitation datasets for 1970-2005 (http://www.cpc.ncep.noaa.gov/products/precip/realtime/GIS/SA/SA-precip.shtml, see also Chen et al. (2008)). Other datasets cover only the Amazon or Brazil (e.g. Shi et al, 2000; Silva et al, 2007), thereby missing the Guiana Shield area altogether. Global datasets (e.g. CMAP, Xie & Arkin, 1997; GPCP, Adler et al, 2003) combine similar sets of limited observations with satellite or model outputs only at a coarse grid-scale (2.5° x 2.5° latitude-longitude grids).

A recent study of the precipitation and temperature regimes of the Guianas (Bovolo et al., 2012) has shown that reanalysis datasets (specifically ECMWF ERA-40, with a 1.125° grid) provide a reasonably good representation of monthly, annual and averaged seasonal temperature across the region when compared with observations. However, the reanalysis data is limited in representing precipitation amounts (Bovolo et al., 2012). The newer ECMWF ERA-Interim dataset offers a better representation of the water cycle due to revisions in the humidity analysis and bias correction for radiance data (Dee et al., 2011) at an increased 0.75° resolution. In a comparison of descriptions of the hydro-climatology of the Amazon basin between ERA-Interim and ERA-40 data and local observations, Betts et al. (2009) found that ERA-Interim remedied substantial drawbacks in the ERA-40 precipitation climatology of the Amazon basin but still suffered from a general dry bias, specifically in the amplitude of the seasonal precipitation cycle, in comparison with local observations. A better spatial resolution is achieved by TRMM (Tropical Rainfall Measuring Mission) satellite observations (grid scale of 0.25°). However, there are uncertainties in the TRMM rainfall anomaly algorithms to predict rainfall (Clarke et al., 2011; Li et al., 2012). TRMM data have been used in Amazonia (Collischonn et al., 2008), but no published studies have yet assessed or used TRMM data in the Guiana Shield region.

The $\delta^{2}H$ and $\delta^{18}O$ isotopic composition of precipitation and inland waters have been applied successfully to understand spatial and temporal patterns of hydrology (Araguas-Araguas et al., 2000; Bohnke et al., 2002; Clark and Fritz, 1997; Craig, 1961; Dansgaard, 1964; Dawson and Simonin, 2011; Fricke and O'Neil, 1999; Gat, 2004; Martinelli et al., 1996; Matsui et al., 1983; Rozanski et al., 1993). In northern Amazonia and the Guianas, the degree of depletion of $\delta^{2}H$ and $\delta^{18}O$ isotopes in precipitation has been attributed to the seasonal displacement of the ITCZ that controls the movement of moist air masses (Bowen and Revenaugh, 2003; Feng et al., 2009; Vuille et al., 2003). Stable water isotopes of inland waters have also been used successfully to determine

water sources, assess the contribution of overland- and base-flows to stream flow, and establish potential rates of evaporation (Martinelli et al., 1996; Saylor et al., 2009; Speed et al., 2011; Strauch et al., 2006; Wassenaar et al., 2011). However, there are few observational data available for this region in the International Atomic Energy Agency-Global Network of Isotopes in Precipitation or Rivers (IAEA-GNIP/GNIR) databases, and most of the available records are very short (Vuille et al., 2003). To compensate for the lack of field-based data in the tropics, various interpolation models have been developed and used to identify monsoonal, altitudinal and seasonal dynamics (Bowen and Revenaugh, 2003; Gonfiantini et al., 2001; Saylor et al., 2009; Sturm et al., 2007; Vuille et al., 2003; Vuille and Werner, 2005), and impacts from deforestation (Bowen et al., 2005; Henderson-Sellers et al., 2002). However, the underlying processes and feedbacks that control regional hydro-climate dynamics of this region are not well constrained.

This study presents first precipitation, hydrology and isotopic chemistry results from 2009 to 2011 for rainforest and the neighbouring forest-savannah transition zone in central Guyana, which represent part of a wider frontier forest that extends approximately 500 km from southern Venezuela to the Guyanese-Brazilian border in the south (Figure 3.1). These results help to address the paucity of field observations in this region, and are compared with data from global models of precipitation and isotopic chemistry to assess whether these models may be used in studies related to hydrological cycles in the region.

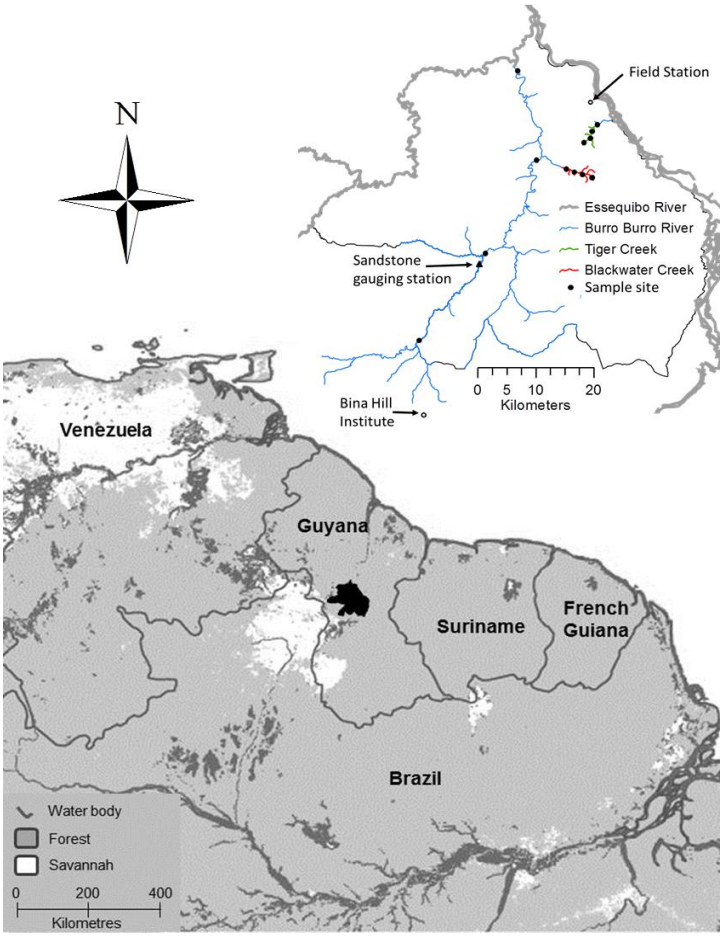

Figure 3.1: Forest coverage of the Guiana Shield (after Gond et al., 2011) with inset of Iwokrama and relevant tributaries of the Burro Burro river catchment and focus catchments.

3.2 Materials and Methods

The Iwokrama rainforest in central Guyana comprises 371,000 hectares (Figure 3.1) and is bounded by the Essequibo River to the East and the Siparuni River, a tributary of the Essequibo, to the west and north (Figure 3.1). It lies just north of the Rupununi savannah wetlands. Iwokrama is situated near the northern extent of the Inter-Tropical Convergence Zone (ITCZ), where there is a transition in the climate regime from north (coastal) to south (savannah) from two wet seasons (primary: May-July and secondary: December-January) and two dry seasons (primary: centred around October and secondary: centred around March) to one wet season (May-August) and one long dry season (September-March) (Bovolo et al., 2012).

The Burro Burro catchment, a tributary of the Essequibo river (the 29th largest river by flow rate in the world (Dai and Trenberth, 2002), covers some 3200 km^2 (Hawkes and Wall, 1993) with approximately 2020 km^2 situated within the Iwokrama Reserve. The main channel of the Burro Burro River bisects the Iwokrama forest, flowing northward from the southern boundary of the forest-savannah transition, forming an approximate 65 km riverine transect. The topography of the catchment ranges from 52 to 995 m above sea level and incorporates a combination of low-lying undulating plains and steeper ranges of the Pakatau hills and the Iwokrama and Turtle mountains (Hawkes and Wall, 1993). Within the Iwokrama rainforest, two small-scale, lowland headwater catchments were studied; each approximately 5-6 km in length with an estimated catchment area of about 15-20 km^2. These 'focus' catchments are located adjacent to each other, and discharge into the Burro Burro River (Blackwater Creek) and directly into the Essequibo River (Tiger Creek). Both focus catchments are situated on similar acid-intermediate volcanic geology, overlain with highly-leached, quartzite, brown and white sands and an approximate 100 mm humic surface layer, with similar forest types including Greenheart (*Chlorocardium rodiei*), Black Kakaralli (*Eschweilera subglandulosa*) and Wamara (*Swartzia leiocalycina*).

One notable difference between the catchments is that the Tiger Creek catchment was harvested for commercial timber species from 2007 to 2009 using reduced impact-logging (RIL) techniques, removing approximately 400 trees. When compared with conventional clear-fell logging techniques, the impact of RIL upon a forest ecosystem is significantly mitigated by reducing the number of trees damaged during logging and aiding ecosystem recovery rates (Macpherson et al., 2012; Macpherson et al., 2010; Miller et al., 2011; Pinard and Putz, 1996).

3.2.1 *Installation*

A new hydro-climate and geochemistry monitoring programme was established in March 2010. Here, we present results from new equipment, together with some pre-existing storage raingauges. A new automatic weather station (AWS; Casella CEL, Bedford, United Kingdom) was installed within the Iwokrama forest approximately 80 km from the rainforest-savannah boundary. This complements a pre-existing manual storage rain gauge (127 mm diameter) in the savannah lands of Annai to form a north-south meteorological transect monitoring the precipitation patterns across a strong change in forest and savannah biomes (Figure 1). Prior to March 2010, total daily rainfall was recorded at Iwokrama Field Station using a standard manual storage rain gauge (127 mm diameter). Where daily rainfall was not recorded (either manually or by the AWS), daily totals were estimated using accumulated measurements from the storage rain gauge.

The two focus catchments were instrumented for stage using DCL 9500 Level Sensors (Gems) calibrated to manual stage board readings. The sensors were housed within a stilling well and connected through a vented cable to a Frog RX data logger (Isodaq Technology). Flows were measured periodically across the range of observed conditions using a StreamPRO ADCP (Acoustic Doppler Current Profiler; Teledyne RD Instruments) at Blackwater Creek, and a Braystoke current meter (Valeport) at Tiger Creek. Rating curves were constructed using these data, and used to convert the monitored stage into flow records for each focus catchment.

3.2.2 *Sampling and analysis for river geochemistry*

To complement the hydro-climate monitoring programme, river water was collected from the main channel of the Burro Burro during the dry and wet seasons (March and July) of 2010 at four in-stream locations forming a north-south transect (Figure 3.1). The focus catchments were sampled from the centre of the river channel during the same dry and wet seasons of 2010 and again in 2011 (March and June/July in each year) from the river source at three locations approximately 1.5 kms apart. In total, four samples were collected from each focus catchment during each season. Sampling dates were: Blackwater Creek on 05/03/2010, 29/07/2010, 25/03/2011, 23/06/2011; Tiger Creek on 03/03/2010, 17/07/2010, 26/03/2011, 22/06/2011; and Burro Burro River on 20-22/03/2010, 10-12/07/2011. All samples were field filtered using Pall Acrodisc 0.45 µm filters, cold stored in Nalgene bottles and shipped to the UK for analysis.

Water samples were analysed for oxygen and hydrogen isotopes. For further information on the analytical methods used see section 2.3.7.

3.2.3 *Modelled precipitation*

Reanalysis datasets offer physically coherent and realistic atmospheric parameters representing available historical observations at a global scale. The ECMWF ERA-Interim reanalysis is derived from modified operational weather forecast and analysis models, run in a retrospective manner (Dee et al., 2011). The precipitation outputs come as a forecast product from a 12-hour analysis cycle, where available observations are combined with prior information from the forecast model to estimate the evolving state of the global atmosphere and at the earth's surface. Although not directly observed, precipitation is constrained by the temperature and humidity information derived from the assimilated observations used to initialise the forecast. ERA-Interim daily precipitation time series data were downloaded from the ECMWF data server for the period 1st Jan 1979 to 31st Dec 2011 (http://data-portal.ecmwf.int/data/d/interim_full_daily) and the two grid cells encompassing the observation area covered by the field based studies were extracted (Figure 3.2).

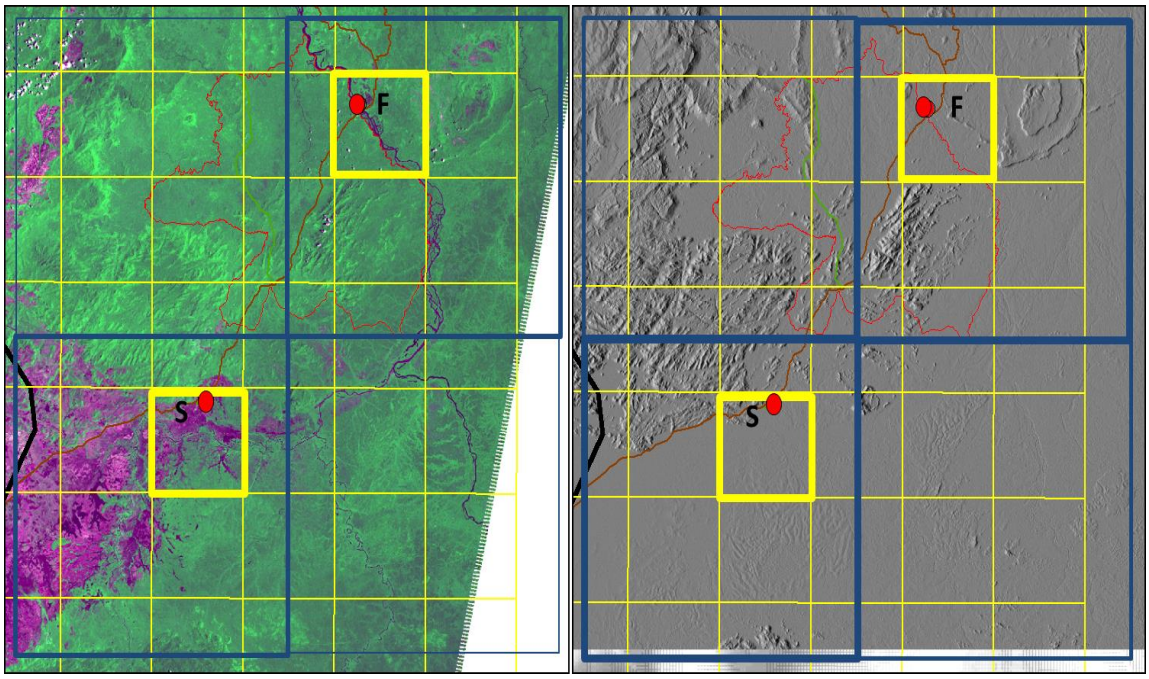

Figure 3.2: (left) Landsat image (derived from http://earthexplorer.usgs.gov/) showing forest vegetation in green and savannah in pink and (right) USGS Earth Explorer GLS-2005 30m resolution digital elevation model map showing relief (downloaded June 2009 from http://edcsns17.cr.usgs/gov/EarthExplorer) overlaid by TRMM grid cells (yellow) and ERA-Interim grid cells (blue). Forest and savannah rain gauges raingauges are labelled F and S respectively. Selected TRMM and ERA-Interim grid-cells are highlighted in bold.

Satellite observations offer the possibility of improved spatial and temporal resolution global estimates of precipitation by direct observation. The TRMM satellite includes precipitation radar, a microwave imager and the Visible and Infrared Radiometer sensors (Huffman et al., 2007). The TRMM multi-satellite precipitation analysis (TMPA) uses combinations of satellite sensors and, where possible, land-surface precipitation gauge analyses in an attempt to improve accuracy, coverage and resolution of satellite based observations and outputs data on a 0.25 x 0.25° spatial resolution in a global belt extending from 50°S to 50°N latitude (Huffman et al., 2007). Algorithm 3B42 produces merged high quality/infrared precipitation and root-mean-square precipitation error estimates on a 3-hour temporal resolution (http://trmm.gsfc.nasa.gov/3b42.html). It combines microwave estimates of precipitation with infrared precipitation estimates calibrated using the microwave precipitation, which are then rescaled to monthly resolution. TRMM version 7a represents a minor correction to TRMM v7. This change is not methodological in nature, but rather corrects for omission of one specific source of microwave data in the original processing of the v7 outputs. TRMM 3b43 v7a monthly gauge adjusted satellite estimates from 1st Jan 2009 to 31st Dec 2011 were extracted from http://reverb.echo.nasa.gov for the two grid cells encompassing the available observations (Figure 3.2).

3.2.4 *δ^2H and $\delta^{18}O$ precipitation maps*

Spatial variability in the δ^2H and $\delta^{18}O$ of precipitation reflects the combination of rainout effects and recycling effects within air masses bringing water vapour to different geographic regions. The largest database of precipitation δ^2H and $\delta^{18}O$ is stored on the Water Isotope System for Data Analysis, Visualization, and Electronic Retrieval (WISER) at http://www-naweb.iaea.org/napc/ih/IHS_resources_isohis.html. This dataset has been used to produce mean monthly δ^2H and $\delta^{18}O$ of precipitation maps for the globe (Bowen et al., 2005). Mean monthly δ^2H and $\delta^{18}O$ precipitation maps were downloaded from http://wateriso.eas.purdue.edu/waterisotopes for the grid cell that covers the Burro Burro catchment.

Table 3.1: Total monthly observed rainfall, and estimates from TRMM and ERA-Interim models from the forest and savannah.

	Forest Iwokrama Field Station (mm)			Savannah Annai (mm)		
	Observed	TRMM	ERA-Interim	Observed	TRMM	ERA-Interim
Jan-2009	199.7[+]	147.4	217.2	176.2	192.9	111.8
Feb-2009	160.4[+]	95.6	113	35.3	53.9	43
Mar-2009	423.5[+]	42.9	124.5	77.3	31.6	46.7
Apr-2009	79.0[+]	174.7	145.1	92.5	85.5	60.2
May-2009	72.9[+]	139.8	44.3	60.7	85.3	17.3
Jun-2009	316.1[+]	299.8	215.7	315.8	290.9	169.7
Jul-2009	411.1[+]	307.7	218.8	421	368.2	208.7
Aug-2009	121.5[+A]	122.4	165	214.2	111.7	166.2
Sep-2009	38.5[+]	101.1	80.6	113.2	29.1	62.4
Oct-2009	121.2[+]	62.1	116	71.1	81.5	62.6
Nov-2009	43.1[+A]	35.1	118.5	107	36.2	67.3
Dec-2009	114.3[+A]	134.3	129.1	155.4	104.1	48.6
Jan-2010	116.4[+A]	95.7	71.8	95.5	33.8	16.3
Feb-2010	82.5[+A]	35.5	57.3	86.3	85.2	22.4
Mar-2010	128.0[M+A]	59.3	111.6	124	63.7	49.1
Apr-2010	412.4	232.6	192.2	425.3	189.9	155.9
May-2010	684.8	390.4	305.1	477.7	338	280.5
Jun-2010	494.2	322.4	273.0	524.7	299	237.5
Jul-2010	450.4[MA]	345.4	292.7	387.3	418.2	259.7
Aug-2010	368.8[MA]	388.1	231.4	500.2	293.3	244.8
Sep-2010	178	85.3	172.4	267.4	104.3	149.8
Oct-2010	112	50.3	118.6	61.7	39.9	104.1
Nov-2010	162.0[M]	149.2	175.6	197.3	81.7	131.7
Dec-2010	152.7[M]	194.1	152.2	170.4	103.9	91.7
Jan-2011	123.8	84.2	93.4	118.1	50.5	50.3
Feb-2011	185.5	259	127.6	62.1	77.3	56.5
Mar-2011	312	394	177.5	247.2	173.1	91
Apr-2011	111.5	53.2	73.3	75.8	24.5	32.5
May-2011	661.5	496.5	315.7	480.3	454.9	306.4
Jun-2011	312	363.7	288.3	691.9	352.7	285.1
Jul-2011	318	297.3	255.0	479.9	242.6	232.2
Aug-2011	144	161	197.2	278.8	200.5	166.5
Sep-2011	100.5	87.4	176.6	127	87.5	180.4
Oct-2011	149	138.1	169.8	119.5	89	149.1
Nov-2011	112	88.7	174.1	39.1	70.8	138.3
Dec-2011	116.5	138.6	125.6	10.1	18.8	67.7

[M]missing data in month, [+] storage rain gauge measurement, [A]approximated with tipping bucket and storage gauges

3.3 Results

3.3.1 *Observed precipitation*

Monthly rainfall totals from January 2009 to December 2011 (Table 3.1 and Figure 3.3) in the forest, generally demonstrate a strong primary wet season from May to August in the forest and primary dry season beginning at the end of September (100 mm/month used as the indicator of a dry season, after Sombroek (2001)). Although a secondary wet-season in November is common on coastal regions (Bovolo et al., 2012), our data for the rainforest shows only small increases in rainfall during this period, but with very wet March months in both 2009 and 2011. A short secondary dry season was observed in April 2009 and 2011 before the primary wet season. In 2009, the primary wet season was shorter with less rainfall in May than 2010 and 2011. Annual rainfall totals (2101, 3342 and 2646 mm for 2009. 2010 and 2011, respectively) show that 2009 was relatively drier, than 2010 and 2011. This precipitation pattern is in contrast to the intense, longer than normal rainy season recorded in the northern and north-western Amazon basin in 2009, which caused extreme flooding (Marengo et al., 2012) and the drought in central Amazonia in 2010 (Lewis et al., 2011; Marengo et al., 2011b).

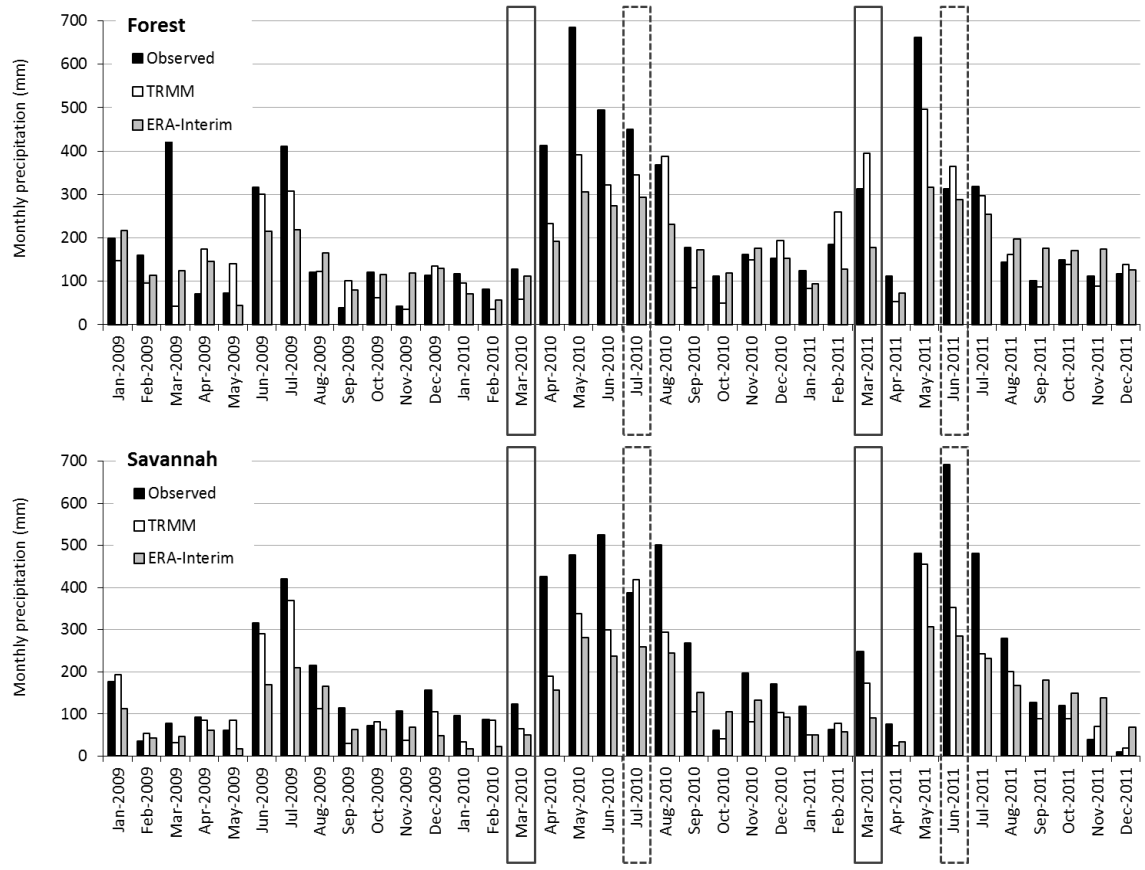

Figure 3.3: (top) monthly rainfall in the forest and (bottom) bordering savannah with sampling events from 2010 and 2011highlighted (solid line dry season; dashed line wet season).

The overall seasonal weather pattern in the savannah, less than 10 km from the rainforest-savannah boundary (Table 3.1 and Figure 3.3) was comparable to the forest with the primary wet season occurring from May to June and the primary dry season beginning in October. However, the savannah did not receive pronounced wet March months in 2009 and 2011, although the 'secondary wet-season' centred in November is still recognisable. Annual rainfall totals (1849, 3318, 2730 mm over 2009, 2010 and 2011 respectively) in the savannah show that it was much drier than the rainforest in 2009 and was classed locally as a drought, whilst 2010 was much wetter than 2012 with severe flooding.

3.3.2 *Modelled precipitation*

Tropical rainforests experience high amounts of convective rainstorms which can lead to high spatial variability. Therefore comparisons of point rain-gauge observations with modelled grid cells, which are representative of an averaged area, are not likely to give good results unless the rain gauge location is representative of conditions over a wider area. To assess the spatial representivity of the new AWS dataset, a comparison was made against a tipping-bucket raingauge at a similar elevation, located within the forest approximately 9 km away. The datasets show that although precipitation between gauges vary spatially on a daily timescale, rainfall over a monthly timescale is similar at both locations (R^2 = 0.88 based on a 17 month time-series between 2010 and 2012). Total rainfall recorded in the rainforest over these 17 months was 5034 mm compared with 5991 mm at the raingauge 9 km away, representing a difference of approx. 17% (note that one rainstorm event was responsible for 532 mm difference in one month). At the larger grid-scale used by ERA-Interim, there is little variation in relief or land cover (thick blue box in Figure 3.2). However, there are some relatively small mountain ranges with elevations from 80-800 m that exist south of the AWS raingauge which make the average relief of the ERA-Interim grid cell slightly higher than at the raingauge location. This may cause modelled precipitation to appear slightly higher than actually observed due to orographic forcing.

In the savannah, comparison of our manual storage raingauge with a tipping bucket raingauge located approximately 3 km away gives a correlation coefficient of 0.85 from 18 months of data between 2010 and 2011, with total rainfall of 4131 and 4948 mm respectively, a difference of approx. 18%. The slightly lower correlation is attributed to differences in the collection methods (i.e. manual vs. tipping bucket) and to the use of

accumulated precipitation values over certain days in the manual time-series, which may have errors from evaporative losses. As seen in Figure 3.2, the 'savannah' raingauge is near several small 'forest-islands' and is partly surrounded by the rainforest-savannah boundary, which extends around the area. The raingauge therefore characterises land cover of approximately 50% savannah and 50% rainforest which is comparable to the larger areas represented by the TRMM and the ERA-Interim grid cells. In terms of elevation, the area south of the raingauge has low relief and low elevation and we therefore assume that the raingauge location is representative of the TRMM grid cell. To the north of the raingauge, there are some small mountainous areas that suggest the ERA-Interim grid cell has a higher average elevation than at the raingauge location. It would therefore be expected that the ERA-Interim dataset may slightly overestimate rainfall in this grid-cell. Changing of the prevailing winds from the north-east, east or south-east, depending on the location of the ITCZ (Bovolo et al., 2012), may also cause a rain shadow of the grid-cell but these local effects should be captured by the raingauge.

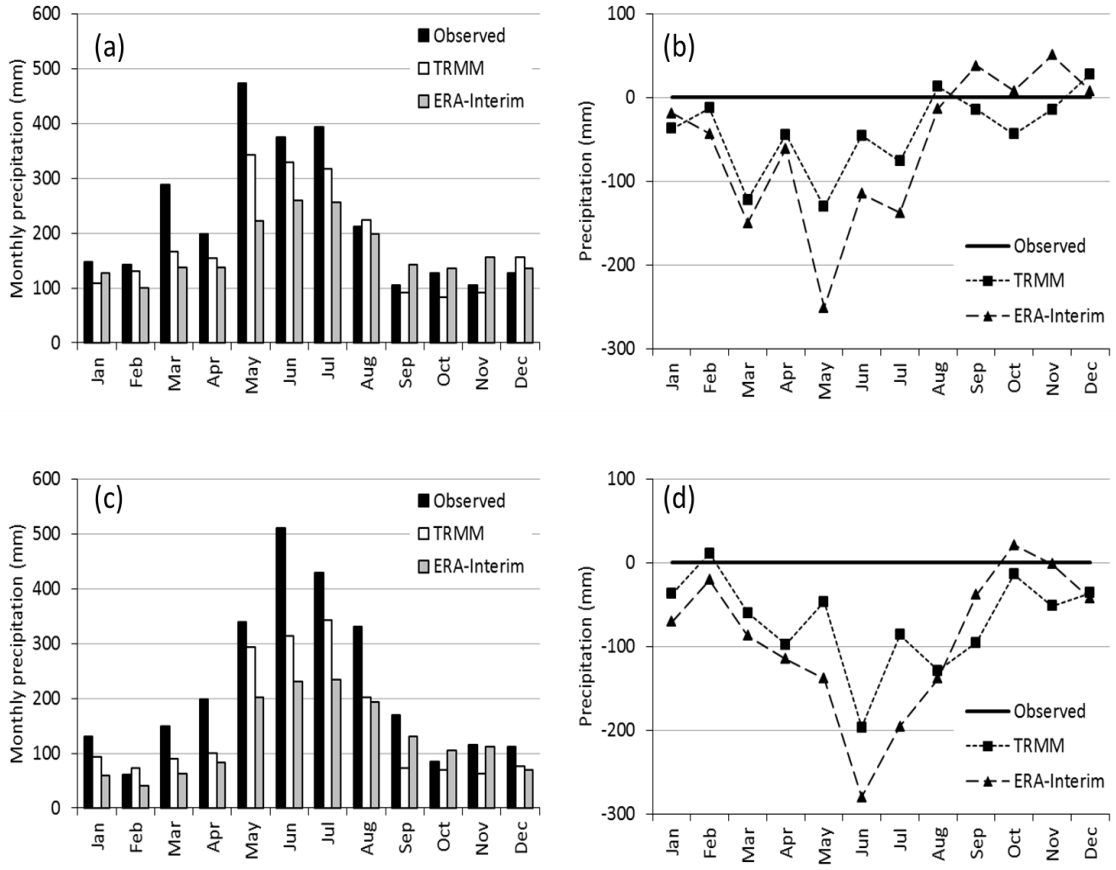

Figure 3.4: Comparison of measured monthly precipitation averaged over 2009-2011 against TRMM and ERA-Interim datasets for the forest (a and b) and savannah (c and d). Plots a and c display recorded values. Plots b and d show the difference between the observed and modelled data.

The TRMM and ERA-Interim data capture a similar precipitation pattern to the observed 2009-2011 data sets with increased precipitation from May to August associated with the primary wet season. However, both models significantly underestimate the precipitation recorded at the forest and savannah sites, especially in the primary wet season; and the ERA-Interim overestimates rainfall slightly in the secondary wet season (Figure 3.4). In the primary wet season of the 2009 'dry' year, TRMM underestimates observed rainfall by 5 to 25% for the rainforest and 8-48% in the savannah. In the 2010 and 2011 'wet' years this discrepancy is more pronounced, with rainfall underestimated by 7-43%, and 5-50% in the rainforest and savannah, respectively. ERA-Interim fares worse, underestimating rainfall in the primary wet season by 22-72%, 33-55% and 8-59% in 2009, 2010 and 2011, respectively. Both datasets also overestimate precipitation in the dry season from September to December but the ERA-Interim dataset is most pronounced overestimating observed precipitation by 6-175%. In total, over the 3 years, ERA-Interim rainfall underestimates rainfall by 53% in the forest and 58% in the savannah, whilst TRMM underestimates rainfall by 43% in the forest and 56% in the savannah.

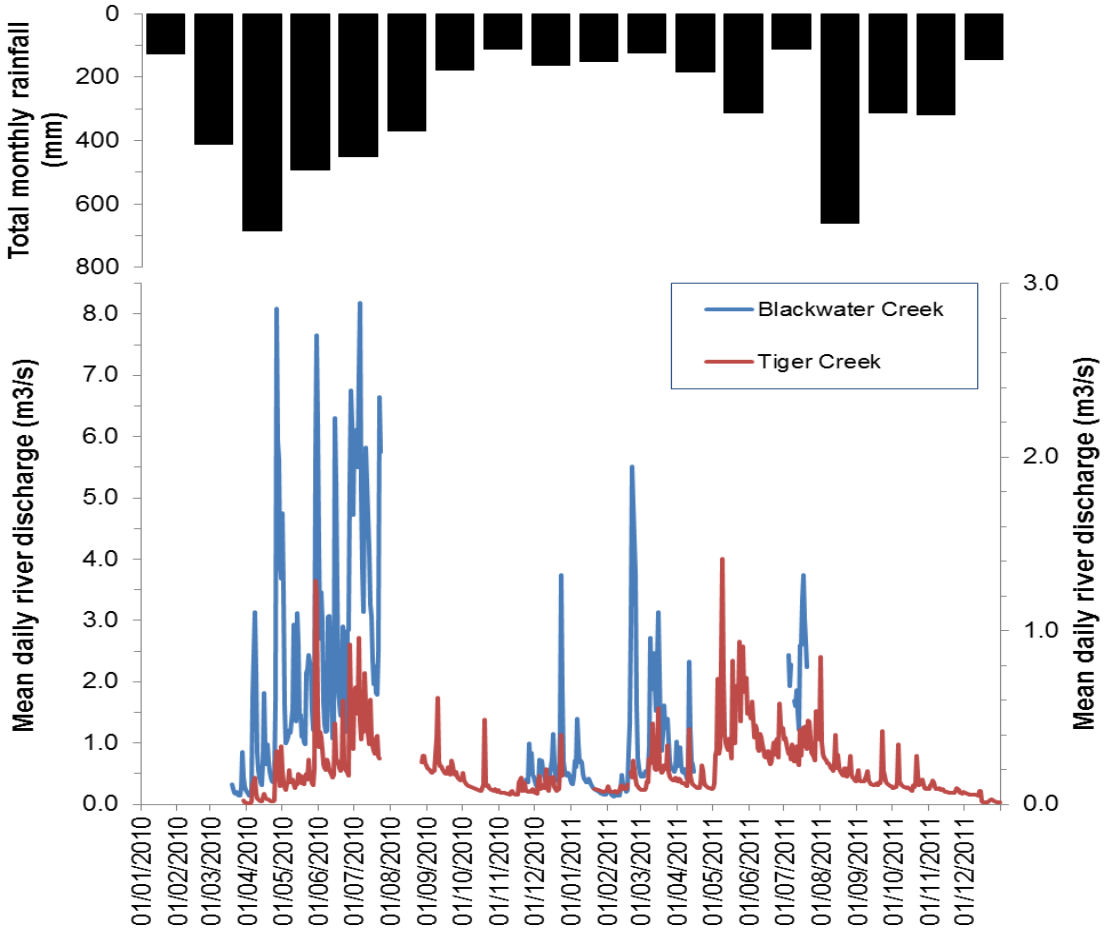

Figure 3.5: River discharge of Tiger and Blackwater Creek from March 2010 to July 2011.

3.3.3 *River hydrology*

Monthly averaged river discharges for Blackwater and Tiger Creek are presented in Table 3.1 and Figure 3.5, providing the context for river geochemical sampling. A near complete time series record for Tiger Creek exists from the end of March 2010 to December 2011 with gaps from the end of July to the end of August 2010 and the end of December 2010 to mid-February 2011, due to instrument failures. Continuous records for Blackwater Creek are only available from end of March to end of July 2010 and end of November 2010 to mid-March 2011, again due to instrument malfunction. Blackwater Creek has a higher and flashier flow than Tiger Creek, with discharges ranging from 1-8 m^3/s, whereas Tiger Creek discharges rarely reach over 1 m^3/s.

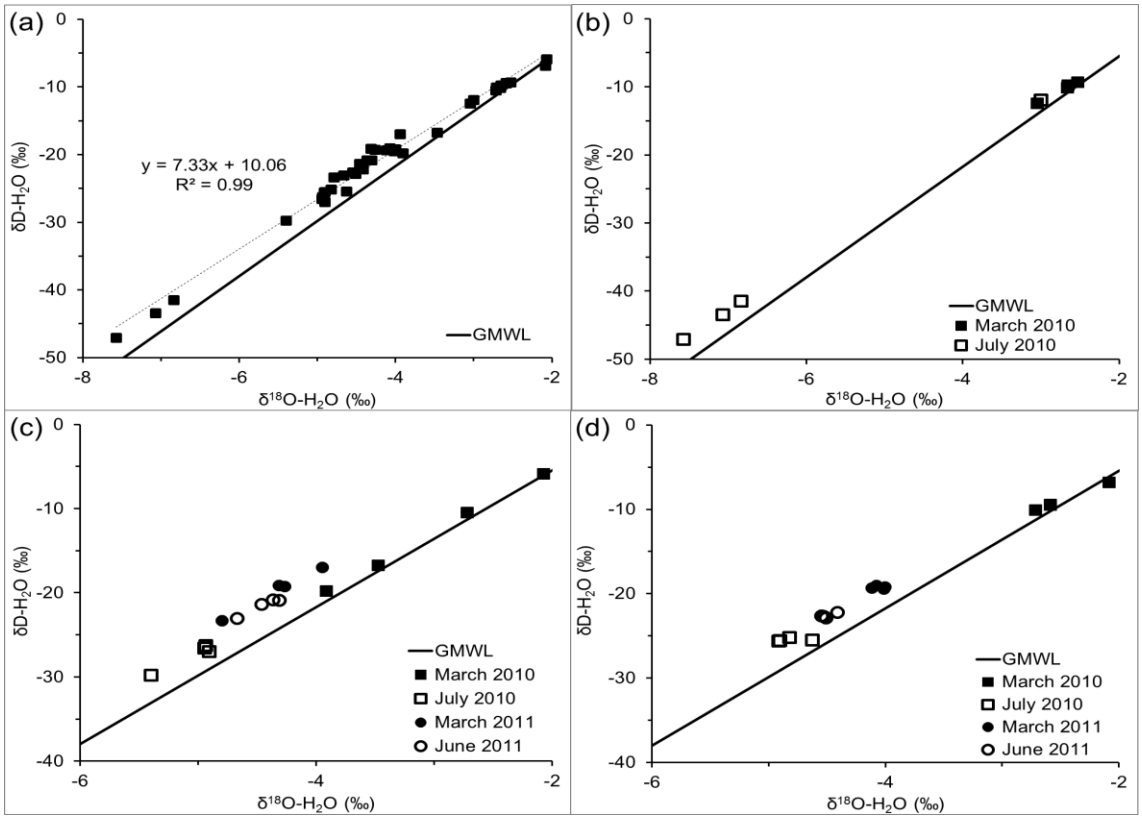

Figure 3.6: δ^2H and $\delta^{18}O$ values of water plotted against the global meteoric water line (GMWL) of: (a) all river water samples, (b) Burro Burro River 2010, (c) Tiger Creek 2010-2011, (d) Blackwater Creek 2010-2011.

3.3.4 *River geochemistry*

Water isotope analyses were conducted on 40 river water samples (Table 3.2). The δ^2H and $\delta^{18}O$ values are plotted together with the Global Meteoric Water Line (GMWL, Craig, 1961; Rozanski et al., 1993) in Figure 3.6a. The overall ranges of the δ^2H and $\delta^{18}O$ values are -47 to -5.9‰ and -7.6 to -2.1‰, respectively. Generally, the dataset plots along or near the GMWL with a correlation coefficient of 0.99 and a slope of 7.33.

The Burro Burro River water displays a change in isotopic signature from March (very dry) to July (wet month following a very wet period) during 2010. March samples display isotopic ranges of δ^2H from -12.4 to -9.3‰ and $\delta^{18}O$ of -3.0 to -2.5‰. In July, with the exception of one sample located at the southern extent of the sampling transect (δ^2H = -11.9‰ and $\delta^{18}O$ = -3‰), a decrease in the δ^2H and $\delta^{18}O$ values in downstream samples is observed with ranges of δ^2H from -47 to -41.5‰ and $\delta^{18}O$ of -7.6 to -6.8‰ (Figure 3.6b).

Table 3.2: Water isotope values (δ^2H and $\delta^{18}O$) of river water collected during dry and wet seasons in 2010 and 2011.

	March 2010 Dry Season		**July 2010 Wet Season**		**March 2011 Dry Season**		**June 2011 Wet Season**	
Sample Site	**$\delta^{18}O$** (‰)	**δ^2H** (‰)	**$\delta^{18}O$** (‰)	**δ^2H** (‰)	**$\delta^{18}O$** (‰)	**δ^2H** (‰)	**$\delta^{18}O$** (‰)	**δ^2H** (‰)
Burro Burro River	-2.7	-10.1	-7.1	-43.4	-	-	-	-
	-2.7	-9.7	-6.8	-41.5	-	-	-	-
	-2.5	-9.3	-7.6	-47.0	-	-	-	-
	-3.0	-12.4	-3.0	-11.9	-	-	-	-
Tiger Creek	-3.9	-19.8	-4.9	-27.0	-4.3	-19.3	-4.4	-20.8
	-2.7	-10.5	-4.9	-26.5	-3.9	-17.0	-4.5	-21.3
	-3.5	-16.7	-4.9	-26.3	-4.3	-19.1	-4.3	-20.9
	-2.1	-5.9	-5.4	-29.8	-4.8	-23.3	-4.7	-23.0
Blackwater Creek	-2.7	-10.1	-4.9	-25.5	-4.0	-19.5	-4.5	-22.8
	-2.6	-9.5	-4.9	-25.6	-4.0	-19.2	-4.5	-22.6
	-2.6	-9.4	-4.6	-25.5	-4.1	-19.0	-4.4	-22.2
	-2.1	-6.8	-4.8	-25.1	-4.1	-19.3	-4.6	-22.6

The focus catchments display a similar isotopic pattern from March to July 2010 as observed for the Burro Burro. However, isotopic differences between March (relatively wet month in the dry season) and June (relatively dry month following a wet period) 2011 are not as distinct, with data points more clustered (Figure 3.6c and 6d). The June/July results of Blackwater Creek catchment (Figure 3.6d) in both 2010 and 2011 are relatively constant between years and clustered (within 3‰ δ^2H and 0.5‰ $\delta^{18}O$ ranges). The ranges of values for δ^2H and $\delta^{18}O$ from samples collected in 2010 and 2011 are higher in March (up to 19.0 and 2‰ respectively) compared with June/July. The Tiger Creek 'managed' catchment results (Figure 3.6c) have a similar isotopic pattern to the Blackwater Creek pristine catchment in June/July of 2010 and 2011. However, a wider scattering of the Tiger Creek data along the GMWL compared with the Blackwater Creek data is observed in the March results of both years with the greatest range seen in 2010 (δ^2H: -19.8 to -5.9‰ and $\delta^{18}O$: -3.9 to -2.1‰).

3.4 Discussion

3.4.1 *Precipitation patterns observed across the forest and savannah of central Guyana compared with TRMM and ERA-Interim models (2009-2011)*

Our new climate records from central Guyana are the first published data from this understudied area. A distinct seasonal pattern in rainfall was observed in the forest of Iwokrama between 2009 and 2011, with the peak wet season occurring between May and August and the peak dry season starting in late August. Our field data further show that the secondary wet season that normally occurs around November was more variable, with March being particularly wet in two of the three years (Figure 3.3). Rainfall records from the savannah-rainforest boundary show similar amounts of total monthly rainfall compared with the rainforest, although dry season totals are more variable. There are only small differences in the monthly totals of precipitation between the forest and savannah, indicating that the properties of the air masses crossing the region are not significantly modified by the change in land cover across the spatial scale considered here. The three years of data capture large inter-annual variability. An anomalous southerly shift of the ITCZ has been identified as the cause of the May-June 2009 Amazonian floods (Marengo et al., 2012), and this is also linked to the reduced rainfall in Guyana during these months. Conversely, the anomalous migration of the ITCZ to the north in March-May 2010 caused the 2010 central Amazonian drought (Lewis et al., 2011; Marengo et al., 2011b), and is also linked with the prolonged wet season in Guyana during these months.

The point-scale seasonal pattern of rainfall observed in the forest is broadly consistent with results from grid-scale TRMM and reanalysis data for both ERA-Interim (this study) and ERA-40 (Bovolo et al., 2012). However, the actual amounts of precipitation are greatly underestimated in the peak wet season (both datasets) and overestimated in the dry season (ERA-Interim). ERA-Interim uses temperature, humidity and radiance data to forecast precipitation, which is therefore only indirectly constrained by observations (Dee and Uppala, 2009; Dee et al., 2011; Simmons et al., 2010). In the Amazonia and Guiana region, approximations used in the model's representation of moist processes are not well constrained because of relatively few observations. Consequently, this causes difficulty in modelling convection at coarse spatial scales (Kendon et al., 2012) and affects the quality and consistency of the modelled hydrological cycle (Dee et al., 2011). This is also a problem for Global Climate Models (GCMs), as they tend to depict a relatively weak ITCZ that extends southwards of its

observed position, resulting in poor matches with observed precipitation in tropical regions (IPCC 2007). This makes determining forest vulnerability of Amazonia and the Guiana Shield to climate change difficult (IPCC 2007). TRMM monthly gauge adjusted satellite estimates at a fine grid-scale resolution are generally better at estimating rainfall, although again rainfall is underestimated in the wet-season at our sites. Given that TRMM data is based on satellite observations that are calibrated with available ground observations it should provide a more realistic precipitation estimate than reanalysis data. Previous studies (de Angelis et al., 2004; Franchito et al., 2009) focusing specifically on the "precipitation radar" component of TRMM found that the satellite data product captures important characteristics of rainfall over the Amazon, but rainfall regimes in less humid climates were less well represented. For combined (multi-sensor) rainfall products in an earlier version (v5) of TRMM, Adler et al. (2000) found a dry bias compared to the Global Precipitation Climatology Project (GPCP) dataset. The TRMM family of spatial precipitation data products was designed primarily to study the convective precipitation dominant in the tropics and sub-tropics. The incorporation of imagery from geostationary satellites (e.g. GOES) to estimate rates of precipitation from observations of cloud top temperatures is particularly suited to convective precipitation rather than (large-scale) stratiform precipitation. Nevertheless, the less frequent rates of observation (overpass/revisit frequency) of the passive microwave and space-borne precipitation radar used to calibrate the continuous precipitation estimates from geostationary imagery do limit the coherence/consistency of the multi-sensor approach to remote sensing-derived precipitation estimates (Clarke et al., 2011; Collischonn et al., 2008; Dias De Paiva et al., 2011; Dias Paiva et al., 2011)..

3.4.2 *Residence times of water within the Burro Burro Catchment*

The peak wet and dry conditions of the region from 2010 and 2011 are captured in the $\delta^{2}H$ and $\delta^{18}O$ records of river water (Figure 3.6) with the most distinct differences between the extreme dry and wet seasons of 2010. The riverine signatures show a notable seasonal isotopic separation that is broadly consistent with the rainfall pattern modelled for the Iwokrama region using the interpolated GNIP datasets by Bowen et al. (2005) (Figure 3.7). TRMM images confirm that the spatial positioning of the ITCZ was likely to be responsible for the isotopically lighter water received by river catchments during the peak wet season (Figure 3.8).

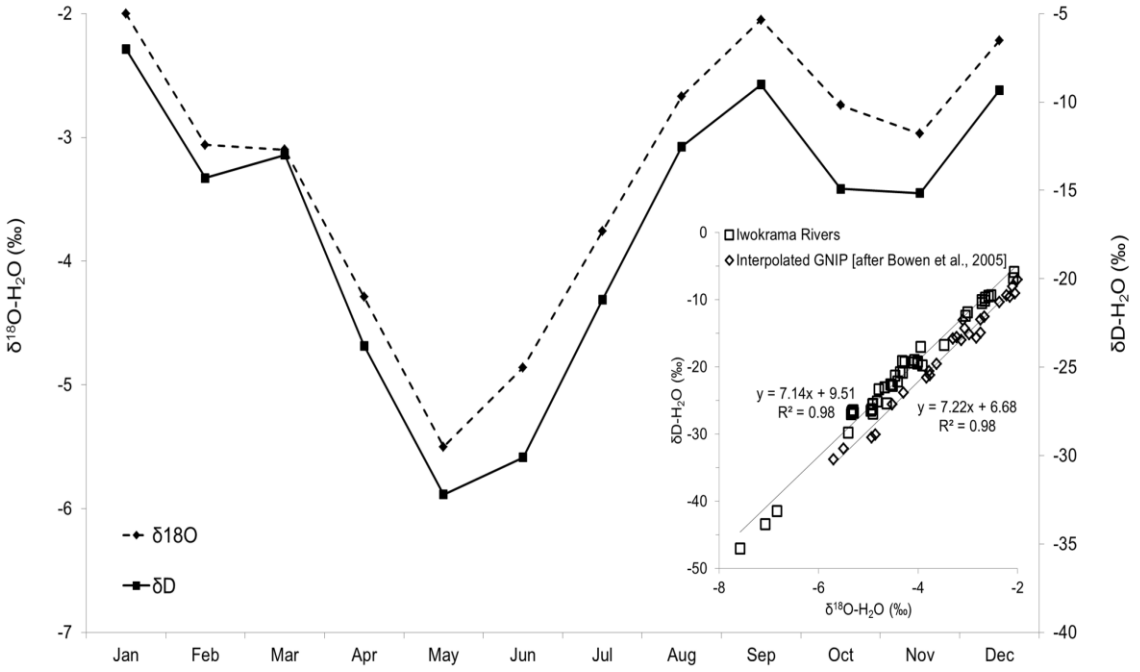

Figure 3.7: Interpolated annual isotopic distribution of δ^2H and $\delta^{18}O$ values of rainfall for the Iwokrama region with insert of interpolated rainfall isotope values compared against riverine water isotopes collected from 2010-2011(after Bowen et al. 2005)

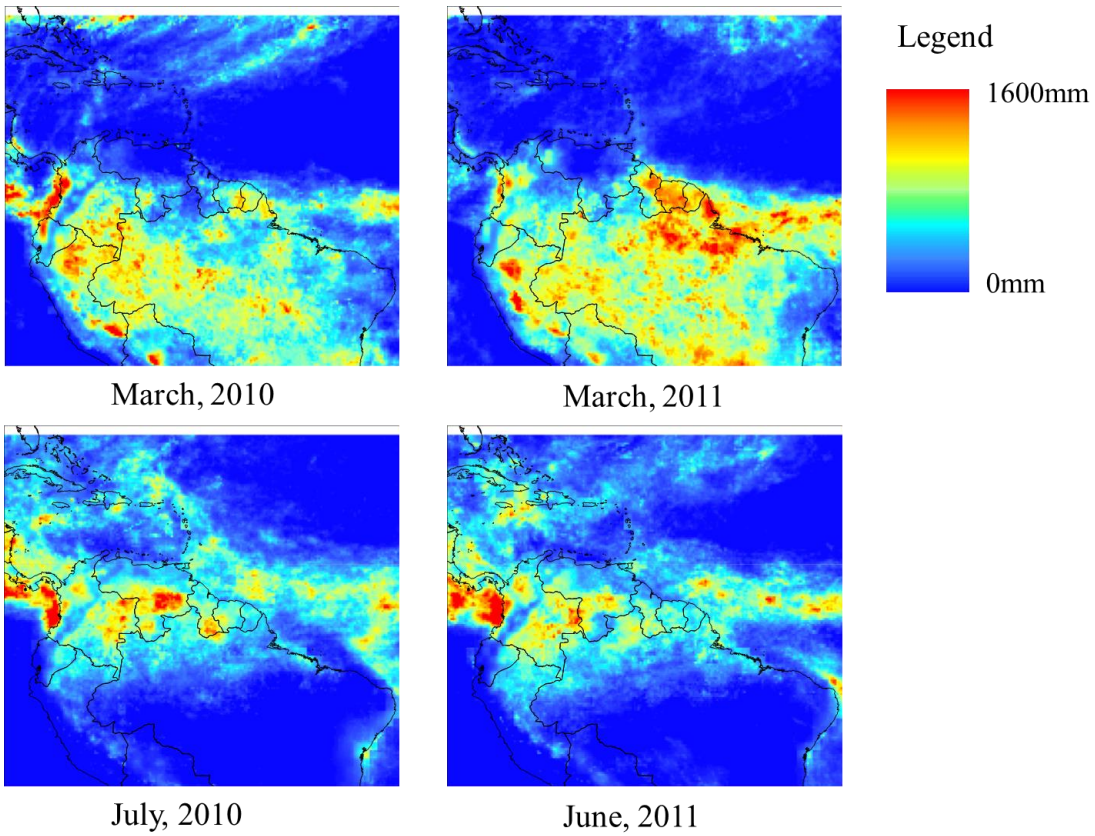

Figure 3.8: TRMM images extracted for the Iwokrama region from March and July, 2010 and March and June 2011 coinciding with river δ^2H and $\delta^{18}O$ isotope datasets.

Although the river δ^2H and $\delta^{18}O$ datasets are much more variable, this is probably a result of localised effects such as evaporation and a mixing of surficial runoff and baseflow waters. Given the observed seasonal pattern in riverine δ^2H and $\delta^{18}O$ signatures, it suggests that the 'amount effect' (Dansgaard, 1964), which brings isotopically lighter water associated with tropical rains of the ITCZ, is the controlling factor in determining wet season isotopic signatures of river water in the region. This is consistent with other studies from Amazonia (Martinelli et al., 1996; Matsui et al., 1983; Rozanski and Araguás-Araguás, 1995; Salati et al., 1979). A notable exception exists for the uppermost section of the Burro Burro River during the wet season of 2010 (close to the savannah-rainforest transition) that exhibits a similar isotopic signature to the dry season (upper right hollow square in Figure 3.6a). This suggests that the rivers draining the upper catchment of the Burro Burro River were not influenced by the ITCZ rains from the north at this time, which is difficult to discern from TRMM datasets alone.

At the small scale, there are no observed differences in δ^2H and $\delta^{18}O$ values between Blackwater and Tiger Creek catchments, suggesting that there is little observable variation in the hydrological cycle from RIL practices (for example, due to evaporation changes as a result of RIL practices). Interestingly, given that the same rainfall totals are recorded in the forest for March and June 2011, there is a notable difference of the δ^2H and $\delta^{18}O$ values in the small scale river catchments. This suggests that differences in the riverine isotopic signatures may capture the preceding hydrological conditions, as would be expected. If so, this time-lag in the hydrological system implies that even at the small-scale there is evidence of a residence time or 'hydrological memory' of precipitation, which may be a month or longer. Further analysis of the hydrological data at higher time resolution will be carried out to investigate this in more detail.

3.5 Conclusion

We present new data on rainfall, stream flow, and isotopic composition of headwater catchments in central Guyana. The data provide the first field results showing local hydro-climatic behaviour within the Guiana Shield region of northern Amazonia during the period from 2009 to 2011, when anomalous shifts in the ITCZ created exceptionally dry and wet periods during 2010 and 2011 respectively, in contrast to the floods and droughts experienced in the Amazon basin during the same period.

Comparison of these new results with data from TRMM and ERA-Interim global models of precipitation and climate show that the pattern of seasonality (occurrence and

timing of wet and dry seasons) is broadly represented by these models, supporting the findings of a previous study using the ERA-40 model (Bovolo et al., 2012). However, monthly precipitation totals are not well characterized by either of these models, with the TRMM and ERA-Interim models underestimating total monthly rainfall by up to 50% and 72% respectively during the wet seasons. The TRMM dataset is generally better at characterising the main dry season from September to December but the ERA-Interim model can overestimate precipitation during the dry season by up to 175%. Although local effects, including topographical variability at the sub-grid scale and the random nature of localised convective storms, may account for some discrepancies, there appear to be systematic biases in the modelled data.

The first new records of river discharge and isotopic geochemistry within headwater catchments in the forest reflect the rainfall patterns of the area, with the $\delta^2H/\delta^{18}O$ isotopic values of the river being broadly consistent with the GNIP rainfall interpolation model (Bowen et al., 2005). The position of the Inter-Tropical Convergence Zone (ITCZ) is shown to influence the isotopic composition of river water, with isotopically lighter water derived from the tropical rainfall of the ITCZ dominating during the wet season.

This new dataset from central Guyana provides valuable field hydro-climate observations in a data-scarce region which may become increasingly important as one of the remaining extensive areas of intact tropical forest, and which may also play a critical regional role in transferring moisture from the Caribbean to the interior of Amazonia. Comparisons against global models of rainfall and geochemistry highlight the specific aspects of the data from these models that should be taken into account if they are used for any studies related to the hydrological cycle within this region. This emphasises the need for more field observations in this region to support understanding and assessments of the role of tropical forests in global cycles.

Chapter 4: The source and fate of organic carbon across the terrestrial-aquatic boundary in RIL impacted tropical rainforest: a case study from a paired catchment experiment in central Guyana.

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Abstract

Tropical headwater rivers at the interface between terrestrial and aquatic environments directly respond to changes from climate and land use. We investigate two small-scale tropical rainforest river catchments in a paired catchment experiment to study how the abundance and composition of carbon entering the aquatic environment in lowland tropical rainforest headwaters is changing by examining the effects of reduced impact logging (RIL) practices. We show bulk soil and river water carbon measurements that indicate RIL may have supplied more organic matter to forest soils compared to a control catchment. Bulk radiocarbon ($\Delta^{14}C$) measurements of riverine dissolved organic carbon and organic matter in surface soils and river bed sediments form both catchments show that the majority of carbon is relatively young (60 years BP). However, deeper soils (up to 1 m) from water saturated wetlands show a clear potential for carbon storage with $\Delta^{14}C$ ages up to 1200 years BP. Stable isotopes of young carbon confirm that a majority of OM is fixed by the C_3 pathway with the most enriched $\delta^{13}C$ signatures in soils occurring with age. We therefore suggest that the observed isotopic fractionation between surface and deep soils is likely the result of either biodegradation or different transport processes. Further experimental data investigating the partitioning of OM between soils and water show end member lignin ratios of S:V/C:V and (Ad:Al)v/(Ad:Al)s must be clearly identified to understand effects of land use change on storage, transport and degradation processes of organic matter .

4.1 Introduction

Tropical rainforests are fundamental components of the global carbon cycle accounting for nearly 40% of terrestrial net primary production (Townsend et al., 2011) and containing 17–25% of the carbon in the terrestrial biosphere (Bonan, 2008). River systems draining tropical rainforests are significant drivers of the global carbon cycle, contributing ~64% of the global riverine carbon flux from land to the ocean (Mayorga et al., 2010). Tropical headwater networks cover significant areas of the land surface with 70-80% of the river network made up of small headwater rivers (Gomi et al., 2002). However, at this interface where hydrology mobilises organic matter (OM) from soil, litter layers and vegetation, there remain large uncertainties about the relative lability of different OM pools (e.g. cellulose, hemi-cellulose and lignin) and the timescales at which they are stored, mobilised or degraded (Richey et al., 2011; Schmidt et al., 2011; Trumbore and Barbosa de Camargo, 2009). This is because tropical river catchments are usually investigated at the larger spatial scale (stream order 8-12) that integrates a spatial signal from allochthonous and autochthonous sources over various timescales (e.g. Richey et al., 1990; Stubbins et al., 2010; Townsend et al., 2011) leading to multiple possible interpretations to explain field observations and field-based data (e.g. Telles et al., 2003; Trumbore and Barbosa de Camargo, 2009). It is, however, at the small headwater scale (stream order 1-3) of tropical forests where degradation and transport processes of the OM cycle are most strongly controlled by the hydrological, chemical and physical processes that link local climate and biodiversity with soil and river geochemistry (Coe et al., 2002; Costa et al., 2002; Johnson et al., 2006a; Kaiser and Guggenberger, 2000; McClain et al., 2003).

Recent studies suggest that the Amazonian rainforest faces an uncertain future from increasing pressures of climate and land use change with a predicted rise in temperature and lower rainfall increasing the likelihood of severe droughts (Betts et al., 2004b; Cox et al., 2004; Cox et al., 2008). Whilst rainforests appear to be resistant to seasonal droughts (Huete et al., 2006; Malhi et al., 2008; Saleska et al., 2007), extreme or extended droughts have been shown to double the rate of tree mortality and decrease the amount of above-ground biomass by up to 25% (Brando et al., 2008; Lola da Costa et al., 2010; Nepstad et al., 2007). In turn, this should lead to substantial fluctuations in the mobilisation, transport, processing and deposition of carbon (e.g. Coe et al., 2011; Davidson et al., 2012; Lewis et al., 2009). Despite this general understanding, empirical evidence from headwater regions of tropical river systems is largely absent. This limits

the applicability of models (Wohl et al., 2012) for estimating the effects of small-scale and rapid processes in the regional and global context (Clark et al., 2010; Cole et al., 2007; McClain et al., 2003).

We investigate how the abundance and composition of carbon entering the aquatic environment in lowland tropical rainforest headwaters is changing by examining the effects of reduced impact logging practices in a paired catchment experiment. We use a combined bulk geochemical, isotopic (both stable and radioactive) and lignin biomarker approach to determine the composition and age of carbon in soils, river waters and river bed sediments. This complementary approach enables us to study how surface soils supply OM to the river, over what timescales, and estimate if there is potential for longer-term carbon storage in soils and river bed sediments from these headwater environments.

4.2 Materials and Methods

Iwokrama comprises of 3710 km^2 of rainforest in central Guyana (Figure 4.1) bounded by the Essequibo River to the East and the Siparuni River, a tributary of the Essequibo catchment, to the west and north (Figure 4.1). Iwokrama is situated near the northern extent of the Inter Tropical Convergence Zone (ITCZ), where there is a transition in the climate regime from north (coastal) to south (savannah) of two wet seasons (primary: May-July and secondary: December-January) and two dry seasons (primary: September-November and secondary: February-April) to one wet season (May-August) and one long dry season (September-March; Bovolo et al., 2012).

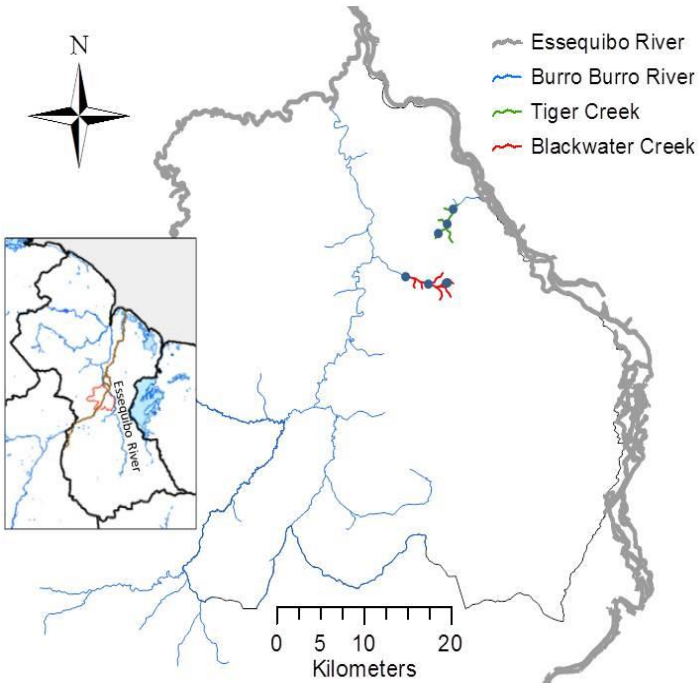

Figure 4.1: The Burro Burro catchment bounded by the Essequibo River and its tributaries to the north, east and west (in grey). The Burro Burro River is shown as a blue line, Blackwater Creek is highlighted in red and Tiger Creek is in green. Blue dots show sampling locations

The Burro Burro catchment, a tributary of the Essequibo River, which is the 10th largest river in South America (Dai and Trenberth, 2002), covers some 3200 km^2 with approximately 2020 km^2 situated within the Iwokrama Reserve (Hawkes and Wall, 1993). Within the Iwokrama reserve, two small, lowland headwater catchments were studied; Blackwater Creek (BWC) is slightly larger at ~20 km^2 and ~6 km long compared to Tiger Creek (TC) which covers ~17 km^2 and ~5 km long. These 'focus' catchments are located within 1.5 km of each other and discharge into the Burro Burro River (Blackwater Creek); and directly into the Essequibo River (Tiger Creek). Both focus catchments are situated on similar acid-intermediate volcanic geology, overlain with highly-leached, quartzite, brown and white sands. They are both dominated by ferralsol soils (under the FAO, 1998 classification system by Deckers et al. (1998)), which is the most common soil of Central Guyana (van Kekem, 1996). The A horizon (0.0 to 0.1 m) is characterised by a typically major sand fraction with high amounts of silt/clay and rootlet material. The underlying sub-soil (0.1 to 1.0 m) is comprised of two sand layers with a minor fraction of silty material adding a brownish colour from 0.1 to 0.4-0.6 m compared to deeper sands (0.4-0.6 to 1.0 m), which are white and saturated, consistent with the Kurupukari sand terraces geological description of central Guyana (Hawkes and Wall, 1993).

Blackwater and Tiger catchments contain similar forest types dominated by greenheart (*Chlorocardium rodiei*), black kakaralli (*Eschweilera subglandulosa*) and wamara (*Swartzia leiocalycina*). However, a notable difference between the catchments is that the Tiger Creek (managed) catchment was harvested for commercial timber species from 2007 to 2009 using RIL techniques, removing approximately 12.5 m^3 of biomass per hectare per 60 year cutting cycle. In total 401 trees were removed from 2007-2009. When compared to conventional clear-fell logging techniques, the impact of RIL upon a forest ecosystem is significantly mitigated by reducing the number of trees damaged during logging and aiding ecosystem recovery rates (Macpherson et al., 2010; Miller et al., 2011).

4.2.1 ***Sampling and analysis***

From Blackwater (control) and Tiger (managed) catchments, river water, river bed surface sediments and riparian soils were collected from three sampling stations approximately 1.5 kms apart. Sample stations were located from the source (site 3) of the focal catchment downstream (site 2 and 1) thus forming an approximate 5 km

transect. Each sample station was sampled during the dry and wet seasons of 2010 and again in 2011 (March and June/July in each year). In July 2010, soil samples were also collected at 0.5 m and 1.0 m below ground level (bgl).

In total, 12 river water, 12 river bed sediment and 21 soil samples were collected from each focus catchment during the project. All water samples were field filtered (0.45 µm Pall SUPOR Acrodisc), measured for spectral absorbance (200-800 nm) using a WPA II Lightwave UV-Vis spectrophotometer (Biochrom) and subsequently kept frozen in Nalgene bottles in the dark. All soils and sediments were stored frozen in pre-cleaned amber glass jars. Water samples were analysed in the laboratory for dissolved organic carbon (DOC), δ^{13}C-DOC, Δ^{14}C-DOC (radiocarbon) and for eight lignin phenol biomarkers; including three vanillyl phenols (vanillin, acetovanillone and vanillic acid), three syringyl phenols (syringaldehyde, acetosyringone and syringic acid) and two cinnamyl phenols (p-coumaric acid and ferulic acid). Soil samples were analysed for total carbon and nitrogen, total organic carbon, δ^{13}C, Δ^{14}C and lignin phenol biomarkers. For a full description of the analytical methods used see section 2.3.

4.3 Results and Discussion

4.3.1 *The distribution of carbon and nitrogen in upper headwater catchments*

Reduced impact logging practices have been shown to alter the water and energy fluxes of rainforests (Fisher et al., 2009; Foley et al., 2003; Malhi et al., 2009), which in turn affect the dynamics of carbon and nutrient cycles at the forest floor (Brando et al., 2008; Davidson et al., 2008; Lewis et al., 2004; Nepstad et al., 2008). This study specifically investigates the carbon (C) and nitrogen (N) pools in the soils, river bed sediments and river water of two small-scale upper headwaters of Guyanese tropical rainforest to examine the impact of forestry activity across the terrestrial-aquatic boundary.

C:N relationships

Whilst the field descriptions are relatively uniform across both sampling transects, bulk C and N concentrations in soils display significant spatial and temporal heterogeneity (Table 2). The TOC content of soils from dry and wet seasons in 2010 and 2011 ranged from 0.27 to 10.35% dwt (n = 24) with the high TOC likely incorporating OM from the above litter layer. N concentrations ranged from 0.03 to 0.58% dwt (n = 24) whilst the C:N ratio ranged from 10.1 to 21.8. The results show that Blackwater Creek generally contains more C and N in its upper headwaters compared to downstream sites, which is

opposite to the managed Tiger Creek where soils increase in C and N. This is generally consistent throughout the dry and wet seasons of 2010 and 2011; however, the pattern reverses in Blackwater Creek for the wet season of 2010 and in Tiger Creek for the dry season of 2011. To further investigate this pattern, the micro-heterogeneity of soils was assessed in both catchments by sampling five sites in duplicate (within 1m of each other). The relative percentage difference (RPD) between these duplicate samples ranged from 3.6 to 21.8% for C and 3.5 to 51.3% for N. The observed variability provides evidence of strong heterogeneity in soils within these settings that is not matched by the relatively homogenous geological conditions. Deeper soils sampled from 0.4 to 1.0 m bgl in the wet season of 2010 show that soil C and N stocks are generally less concentrated compared to surface soils (Figure 4.2 and Table 4.1; C: 0.06 to 1.94% dwt; and N: 0.01 to 0.14% dwt). However, two sites that were water saturated during sampling (2TC and 3BWC) show a contrasting distribution, with relatively stable and enhanced C and N concentrations at depth (Figure 4.2). Assuming that the majority of soil OM is directly supplied from degradation of the above ground litter layer (e.g. Berg and McClaugherty, 2008) and given the spatial and temporal variability of soil C and N concentrations, local biotic factors such as biomass productivity and decomposition rates coupled with variations in water (i.e. soil water content) and sunlight availability must have a large influence on the resulting rate of OM supply to the forest soils (Valentini et al., 2008; Wynn et al., 2006). A likely explanation of the local differences observed here is the small-scale diversity associated with mixed forest, which would supply a variety of different OM types. Gaps in the rainforest canopy may also affect OM decomposition processes by increasing throughfall and light availability at the litter layer (Prescott, 2002; van Dam, 2001). To firmly identify the major factors controlling C and N sequestration in our study region more information including tree density, canopy coverage and leaf litter deposition and degradation rates are required.

In contrast to riparian soils, river bed sediments were more homogeneous (n = 24) in their C and N content. All samples are characterised as white sand and have a narrower range of C and N varying from 0.06 to 3.46% and 0.01 to 0.21% dwt, respectively (Table 4.1), than soils. Despite the lower C and N concentrations in river bed sediments relative to soils, these results emphasise a certain storage potential for both elements, at least temporarily. The C:N ratio of river bed sediments have a wider range from 3.6 to 22.2 compared to soils (10.1 to 21.8), suggesting changes in OM composition with enhanced supply from aquatic or bacterial sources and/or degradation of terrestrial OM.

Table 4.1: Geochemical data from riparian soils, river bed sediments, river water and soil leachate experiments of samples collected from Blackwater (BWC) and Tiger (TC) catchments, central Guyana. Site 3 is the river source with site 2 and 1 downstream, orange rows are dry season samples, white rows are wet season samples (OC organic carbon, N nitrogen, VAL vanillin, VON acetovanillone, VAD vanillic acid, SAL syringaldehyde, SON acetosyringone, SAD syringic acid, CAD p-coumaric acid, FAD ferulic acid, Λ_8 carbon normalised lignin yield, S syringyl, V vanillyl, C cinnamyl, Ad acid, Al aldehyde).

Site	Sample Date	OC	N	C:N	Lignin Phenol Products (mg/100 mg Organic Carbon)									Ratios				$\delta^{13}C$	$\Delta^{14}C$
		(% wt.)	(% wt.)		VAL	VON	VAD	SAL	SON	SAD	CAD	FAD	Λ_8	S/V	C/V	(Ad/Al)V	(Ad/Al)S	(PDB)	
Soil																			
1 BWC	03/10	0.48	0.05	10.3	0.702	0.267	0.509	0.384	0.142	0.241	0.076	0.376	2.699	0.52	0.31	0.73	0.63	-29.26	-
2 BWC	03/10	1.21	0.08	15.9	0.566	0.248	0.458	0.325	0.141	0.189	0.065	0.196	2.187	0.51	0.20	0.81	0.58	-29.00	-
3 BWC	03/10	2.53	0.25	10.2	0.672	0.244	0.357	0.265	0.117	0.150	0.038	0.206	2.049	0.42	0.19	0.53	0.57	-27.97	-
1 BWC	07/10	0.46	0.03	14.2	0.448	0.166	0.311	0.306	0.103	0.143	0.111	0.134	1.723	0.60	0.26	0.69	0.47	-29.13	102.37
2 BWC	07/10	5.42	0.31	17.4	0.550	0.220	0.324	0.422	0.167	0.209	0.067	0.118	2.078	0.73	0.17	0.59	0.50	-29.48	108.28
3 BWC	07/10	1.68	0.13	13.5	0.232	0.086	0.146	0.097	0.036	0.061	0.022	0.067	0.747	0.42	0.19	0.63	0.63	-26.51	93.99
1 BWC	03/11	0.71	0.05	14.1	0.479	0.189	0.226	0.316	0.093	0.128	0.145	0.172	1.748	0.60	0.36	0.47	0.41	-28.94	-
2 BWC	03/11	1.75	0.12	14.9	0.630	0.282	0.375	0.388	0.119	0.180	0.073	0.192	2.239	0.53	0.21	0.59	0.46	-28.94	-
3 BWC	03/11	7.49	0.44	17.0	0.489	0.217	0.290	0.221	0.070	0.112	0.037	0.132	1.568	0.40	0.17	0.59	0.51	-29.31	-
1 BWC	06/11	0.70	0.05	14.6	0.540	0.184	0.357	0.340	0.123	0.148	0.119	0.114	1.925	0.57	0.22	0.66	0.44	-30.76	-
2 BWC	06/11	1.91	0.12	15.8	0.650	0.242	0.478	0.456	0.167	0.241	0.086	0.197	2.517	0.63	0.21	0.74	0.53	-31.02	-
3 BWC	06/11	6.15	0.40	15.4	0.659	0.289	0.418	0.316	0.154	0.206	0.062	0.222	2.325	0.49	0.21	0.63	0.65	-30.27	-
1 TC	03/10	4.07	0.20	20.4	0.483	0.207	0.327	0.305	0.138	0.184	0.063	0.225	1.932	0.62	0.28	0.68	0.60	-28.76	-
2 TC	03/10	1.46	0.08	18.0	0.498	0.206	0.316	0.291	0.119	0.149	0.052	0.183	1.813	0.55	0.23	0.63	0.51	-29.51	-
3 TC	03/10	1.11	0.05	21.8	0.604	0.227	0.360	0.532	0.213	0.254	0.045	0.320	2.555	0.84	0.31	0.60	0.48	-29.43	-
1 TC	07/10	1.78	0.12	15.4	0.221	0.084	0.154	0.156	0.048	0.067	0.034	0.129	0.893	0.59	0.36	0.70	0.43	-28.08	105.33
2 TC	07/10	1.30	0.09	15.3	0.689	0.243	0.374	0.309	0.103	0.138	0.057	0.196	2.109	0.42	0.19	0.54	0.45	-29.67	106.35
3 TC	07/10	1.54	0.09	16.8	0.642	0.250	0.366	0.401	0.153	0.195	0.056	0.161	2.224	0.60	0.17	0.57	0.49	-28.85	109.63
1 TC	03/11	5.03	0.30	16.7	0.314	0.132	0.196	0.191	0.054	0.086	0.022	0.128	1.124	0.52	0.23	0.62	0.45	-29.07	-
2 TC	03/11	10.35	0.58	17.8	0.464	0.196	0.270	0.245	0.090	0.127	0.038	0.117	1.547	0.50	0.17	0.58	0.52	-	-

Site	Sample Date	OC	N	C:N	Lignin Phenol Products (mg/100 mg Organic Carbon)											Ratios		$\delta^{13}C$	$\Delta^{14}C$
		(% wt.)	(% wt.)		VAL	VON	VAD	SAL	SON	SAD	CAD	FAD	Λ_8	S/V	C/V	(Ad/Al)V	(Ad/Al)S	(PDB)	
3 TC	03/11	1.55	0.07	21.3	0.615	0.221	0.215	0.446	0.111	0.134	0.034	0.162	1.938	0.66	0.19	0.35	0.30	-29.10	-
1 TC	06/11	3.61	0.25	14.5	0.257	0.093	0.162	0.153	0.058	0.075	0.020	0.119	0.936	0.56	0.27	0.63	0.49	-30.70	-
2 TC	06/11	3.23	0.16	20.3	0.543	0.192	0.317	0.246	0.094	0.127	0.041	0.265	1.826	0.44	0.29	0.58	0.52	-31.09	-
3 TC	06/11	0.57	0.04	15.9	0.252	0.080	0.120	0.237	0.088	0.081	0.026	0.055	0.940	0.90	0.18	0.48	0.34	-30.90	-
River bed sediments																			
1 BWC	03/10	0.96	0.06	15.5	0.350	0.147	0.271	0.209	0.086	0.136	0.048	0.234	1.480	0.56	0.37	0.77	0.65	-29.09	98.84
2 BWC	03/10	0.81	0.05	15.3	1.063	0.399	0.558	1.044	0.416	0.463	0.155	0.164	4.262	0.95	0.16	0.52	0.44	-29.84	109.85
3 BWC	03/10	0.55	0.05	10.6	0.703	0.281	0.508	0.612	0.260	0.358	0.071	0.207	3.001	0.82	0.19	0.72	0.58	-29.31	108.87
1 BWC	07/10	0.17	0.05	3.6	1.012	0.430	0.807	0.824	0.304	0.478	0.209	0.332	4.396	0.71	0.24	0.80	0.58	-28.87	105.69
2 BWC	07/10	0.21	0.02	9.7	0.592	0.236	0.414	0.339	0.120	0.233	0.045	0.175	2.155	0.56	0.18	0.70	0.69	-29.01	106.78
3 BWC	07/10	1.23	0.07	18.4	0.774	0.283	0.442	0.546	0.198	0.277	0.069	0.174	2.764	0.68	0.16	0.57	0.51	-29.34	108.92
1 BWC	03/11	0.42	0.02	22.2	0.320	0.131	0.200	0.280	0.090	0.139	0.053	0.075	1.288	0.78	0.20	0.63	0.50	-27.69	-
2 BWC	03/11	0.34	0.02	21.5	3.199	1.335	1.882	2.031	0.685	0.823	0.339	0.771	11.065	0.55	0.17	0.59	0.41	-28.70	-
3 BWC	03/11	3.46	0.21	16.5	0.906	0.420	0.569	0.423	0.177	0.239	0.080	0.278	3.093	0.44	0.19	0.63	0.56	-29.47	-
1 BWC	06/11	0.15	0.01	12.3	0.257	0.095	0.238	0.218	0.088	0.159	0.050	0.080	1.186	0.79	0.22	0.93	0.73	-30.83	-
2 BWC	06/11	0.32	0.03	10.7	1.298	0.468	0.804	1.151	0.437	0.597	0.140	0.231	5.125	0.85	0.14	0.62	0.52	-30.86	-
3 BWC	06/11	2.03	0.15	13.2	0.438	0.179	0.337	0.246	0.103	0.167	0.049	0.157	1.675	0.54	0.22	0.77	0.68	-31.54	-
1 TC	03/10	0.37	0.02	17.5	1.475	0.385	0.454	1.276	0.398	0.351	0.088	0.199	4.626	0.88	0.12	0.31	0.28	-28.92	104.34
2 TC	03/10	0.70	0.04	18.8	1.130	0.328	0.390	0.836	0.291	0.283	0.110	0.127	3.495	0.76	0.13	0.34	0.34	-30.13	107.57
3 TC	03/10	0.42	0.03	16.1	0.731	0.235	0.367	0.728	0.268	0.292	0.055	0.167	2.843	0.97	0.17	0.50	0.40	-29.32	104.65
1 TC	07/10	0.07	0.02	4.1	0.355	0.130	0.289	0.388	0.100	0.165	0.060	0.119	1.607	0.84	0.23	0.81	0.42	-27.98	98.84
2 TC	07/10	0.12	0.02	6.8	0.980	0.287	0.496	0.961	0.256	0.319	0.066	0.095	3.461	0.87	0.09	0.51	0.33	-30.35	105.54
3 TC	07/10	0.31	0.03	9.3	1.386	0.460	0.634	1.268	0.405	0.421	0.124	0.163	4.862	0.84	0.12	0.46	0.33	-29.84	106.14
1 TC	03/11	0.12	0.01	12.8	0.521	0.159	0.239	0.375	0.100	0.134	0.053	0.086	1.666	0.66	0.15	0.46	0.36	-27.71	-
2 TC	03/11	1.58	0.09	17.0	0.967	0.363	0.367	0.578	0.165	0.207	0.051	0.151	2.850	0.56	0.12	0.38	0.36	-29.72	-

Site	Sample Date	OC	N	C:N	Lignin Phenol Products (mg/100 mg Organic Carbon)									Ratios				$\delta^{13}C$	$\Delta^{14}C$
		(% wt.)	(% wt.)		VAL	VON	VAD	SAL	SON	SAD	CAD	FAD	Λ_8	S/V	C/V	(Ad/Al)V	(Ad/Al)S	(PDB)	
3 TC	03/11	0.21	0.01	20.8	0.803	0.287	0.329	0.710	0.221	0.255	0.089	0.188	2.883	0.84	0.20	0.41	0.36	-28.83	-
1 TC	06/11	0.06	0.01	5.1	0.442	0.179	0.388	0.344	0.153	0.231	0.093	0.256	2.086	0.72	0.35	0.88	0.67	-30.56	-
2 TC	06/11	0.24	0.02	14.8	0.973	0.320	0.471	0.971	0.353	0.357	0.101	0.168	3.716	0.95	0.15	0.48	0.37	-31.98	-
3 TC	06/11	0.15	0.02	8.5	0.488	0.175	0.317	0.524	0.210	0.243	0.061	0.219	2.237	1.00	0.29	0.65	0.46	-31.59	-
River water																			
1 BWC	03/10	17.00	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-29.79	106.82
2 BWC	03/10	18.50	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-29.68	110.70
3 BWC	03/10	26.43	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-29.45	107.93
1 BWC	07/10	22.07	-	-	0.030	0.021	0.050	0.030	0.018	0.032	0.009	0.007	0.20	0.80	0.15	1.64	-	-29.49	108.68
2 BWC	07/10	28.10	-	-	0.028	0.019	0.041	0.027	0.017	0.023	0.006	0.004	0.17	0.77	0.12	1.47	-	-30.32	108.65
3 BWC	07/10	26.72	-	-	0.014	0.009	0.021	0.014	0.008	0.014	0.004	0.003	0.09	0.83	0.15	1.48	-	-29.95	110.97
1 BWC	03/11	24.47	-	-	0.071	0.050	0.094	0.066	0.037	0.062	0.014	0.012	0.40	0.76	0.12	1.33	-	-22.30	-
2 BWC	03/11	18.37	-	-	0.086	0.066	0.125	0.082	0.048	0.077	0.018	0.014	0.52	0.75	0.12	1.46	-	-26.11	-
3 BWC	03/11	24.78	-	-	0.056	0.041	0.074	0.045	0.025	0.042	0.011	0.008	0.30	0.66	0.11	1.32	-	-23.30	-
1 BWC	06/11	17.13	-	-	0.153	0.111	0.227	0.147	0.089	0.152	0.023	0.022	0.92	0.79	0.09	1.48	-	-29.06	-
2 BWC	06/11	16.87	-	-	0.163	0.115	0.249	0.154	0.091	0.160	0.027	0.026	0.99	0.77	0.10	1.53	-	-29.26	-
3 BWC	06/11	14.97	-	-	0.141	0.103	0.210	0.121	0.075	0.125	0.022	0.017	0.82	0.71	0.09	1.49	-	-28.91	-
1 TC	03/10	6.17	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-30.18	-
2 TC	03/10	10.91	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-29.56	-
3 TC	03/10	56.31	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-29.68	-
1 TC	07/10	42.59	-	-	0.028	0.019	0.041	0.028	0.017	0.024	0.006	0.004	0.17	0.78	0.12	1.46	-	-22.04	107.66
2 TC	07/10	44.62	-	-	0.019	0.014	0.030	0.021	0.013	0.022	0.006	0.005	0.13	0.88	0.17	1.56	-	-20.33	107.75
3 TC	07/10	43.23	-	-	0.034	0.024	0.048	0.036	0.021	0.032	0.009	0.006	0.21	0.83	0.14	1.40	-	-27.09	111.02
1 TC	03/11	20.01	-	-	0.083	0.058	0.105	0.080	0.043	0.071	0.021	0.013	0.47	0.79	0.14	1.26	-	-25.44	109.30
2 TC	03/11	13.03	-	-	0.098	0.073	0.135	0.096	0.051	0.090	0.025	0.017	0.58	0.77	0.14	1.38	-	-27.33	109.03

Site	Sample Date	OC	N	C:N	Lignin Phenol Products (mg/100 mg Organic Carbon)								Ratios					$\delta^{13}C$	$\Delta^{14}C$
		(% wt.)	(% wt.)		VAL	VON	VAD	SAL	SON	SAD	CAD	FAD	Λ_8	S/V	C/V	(Ad/Al)V	(Ad/Al)S	(PDB)	
3 TC	03/11	38.91	-	-	0.068	0.045	0.085	0.069	0.032	0.049	0.016	0.008	0.37	0.76	0.12	1.24	-	-27.46	108.81
1 TC	06/11	21.11	-	-	0.145	0.098	0.190	0.135	0.077	0.118	0.020	0.016	0.80	0.76	0.09	1.31	-	-28.68	-
2 TC	06/11	17.89	-	-	0.115	0.080	0.156	0.133	0.073	0.130	0.021	0.016	0.72	0.96	0.11	1.35	-	-29.15	-
3 TC	06/11	36.46	-	-	0.081	0.056	0.110	0.101	0.051	0.074	0.021	0.009	0.50	0.91	0.12	1.36	-	-28.86	-
Soil leachate																			
1 BWC	07/10	18.65	-	-	0.164	0.118	0.460	0.150	0.100	0.260	0.181	0.200	1.63	0.69	0.51	2.80	-	-	-
2 BWC	07/10	108.03	-	-	0.152	0.092	0.328	0.121	0.074	0.176	0.053	0.035	1.03	0.65	0.15	2.16	-	-	-
1 TC	07/10	25.61	-	-	0.073	0.037	0.267	0.050	0.024	0.127	0.051	0.005	0.64	0.53	0.15	3.65	-	-	-
2 TC	07/10	40.70	-	-	0.190	0.092	0.462	0.134	0.075	0.380	0.050	0.072	1.46	0.79	0.16	2.43	-	-	-
3 TC	07/10	40.90	-	-	0.174	0.105	0.348	0.118	0.081	0.200	0.079	0.075	1.18	0.64	0.24	2.00	-	-	-

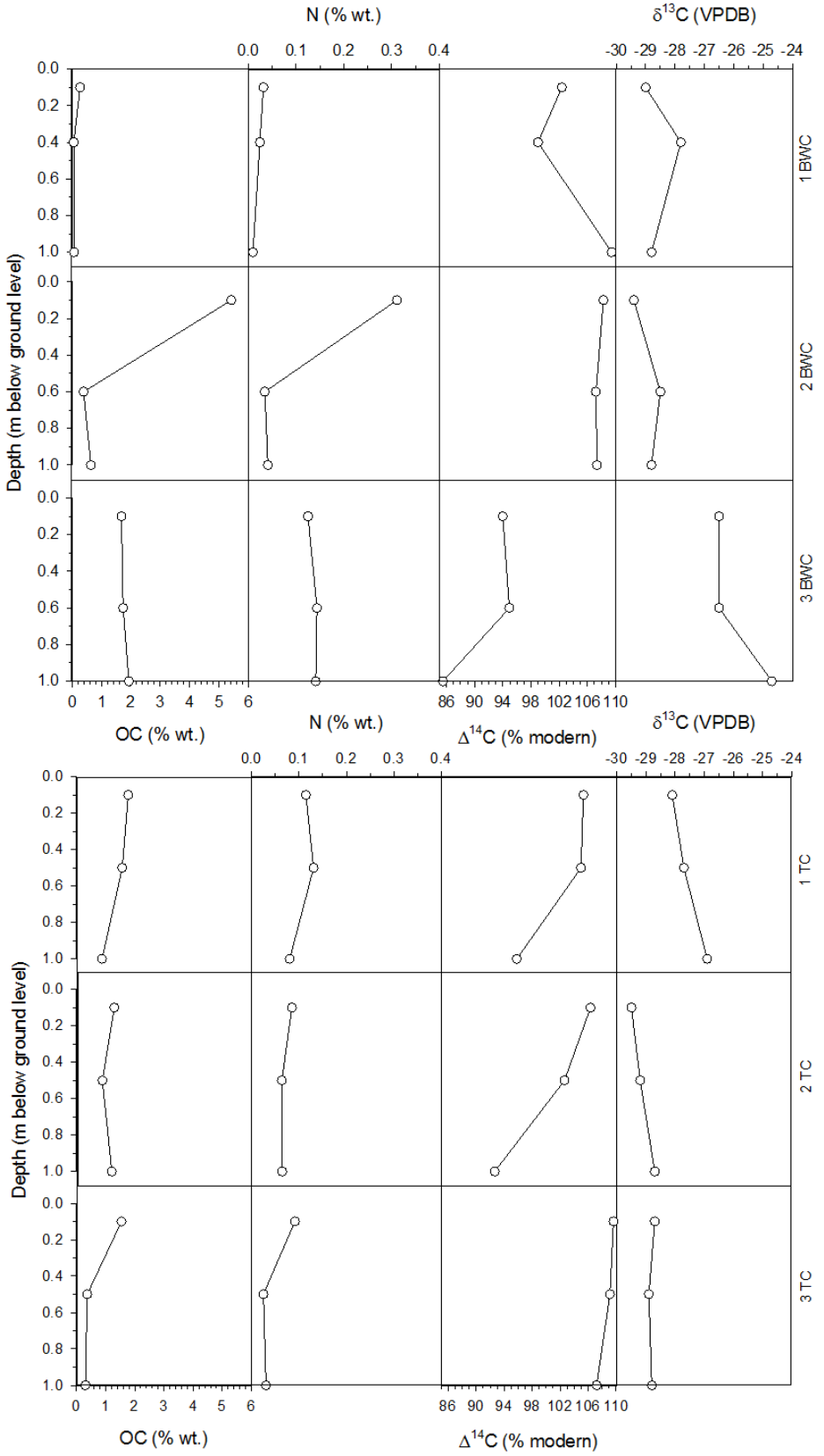

Figure 4.2: Down core profiles of organic carbon (OC), nitrogen (N), $\Delta^{14}C$ and $\delta^{13}C$ of soils collected from six sites at Blackwater (BWC) and Tiger (TC) catchments in July 2010.

Dissolved organic carbon

The transport of carbon from riparian soils into the river was investigating by analysing the DOC content of the river water at the same locations and time as the river bed sediment samples. Previous studies of low latitude tropical rivers (such as the Burro Burro River) have shown that riverine OM transport is dominated by the DOC fraction (<0.45 um) rather than particulate organic carbon (POC >0.45 um) (Huang et al., 2012; Mayorga et al., 2010). Therefore, this study focused on the dissolved fraction of riverine OM. DOC ranged from 6.17 to 56.31 mg/L with higher concentrations observed in Tiger Creek (Table 4.1) than Blackwater Creek. This range of DOC is similar to those reported for upper tributaries of the Orinoco and Congo Rivers (Battin, 1998; Spencer et al., 2012) but higher than those generally reported for the Amazon (Johnson et al., 2006b; Waterloo et al., 2006). The more DOC rich waters of Tiger Creek may indicate that the harvested catchment is releasing more carbon due to RIL activities. However, section 5.3 of this thesis highlights the extreme variability of DOC ranging from ~10 mg/L to ~ 114 mg/L over short temporal scales (13.5 hours) emphasising that caution must be taken when single point riverine measurements are interpreted to characterise temporally variable catchments.

4.3.2 *Lignin as a tracer of organic matter between soil, water and river bed sediments*

Lignin is a complex macromolecule comprised of phenyl-propane subunits linked by a variety of carbon–carbon and ether bonds and are unambiguous biomarkers for vascular plant-derived OM (Hedges and Mann, 1979). The contribution of lignin phenols to the total carbon pool was assessed using yields of lignin oxidation products normalised to organic carbon content (Λ_8; Hedges and Mann 1979). In total, eight lignin phenol CuO oxidation products (Figure 4.3) were identified in soil (n = 24), river bed sediments (n = 24) and river water (n = 18) from the dry and wet seasons of 2010 and 2011 (NB: no water samples were analysed in the dry season of 2010). The Λ_8 ranged from 0.74 to 2.70 mg/100 mg OC for soils and 1.19 to 11.07 mg/100 mg OC for river bed sediments (Table 4.1). River waters ranged from 0.09 to 0.96 mg/100 mg OC (Table 4.1), which is comparable to the reported range for the Congo and Amazon Rivers (Aufdenkampe et al., 2007; Hedges et al., 2000; Spencer et al., 2012). The river bed sediments of both Blackwater and Tiger catchments contain large amounts of lignin compared to soils and river water considering the relatively low amounts of organic carbon in the samples. The increased lignin yield in river bed sediments suggests that phenols are sorbed to and/or co-precipitating with minerals such as Al and Fe hydrous oxides (Gu et al., 1995;

Kaiser, 2003; Scheel et al., 2008a) which are abundant in the surrounding ferralsol soils. The latter mechanism would cause preferential retention of lignin phenols compared to other dissolved organic matter (DOM) components within the total OM pool (Kramer et al., 2012). Furthermore, it would act as a selective preservation mechanism, as once adsorbed or co-precipitated to form an organo-mineral complex, lignin phenols are largely insoluble, have reduced bioavailability and are difficult to desorb without large changes in chemical conditions (Gu et al., 1995; Kramer et al., 2012; Scheel et al., 2008a; Scheel et al., 2008b).

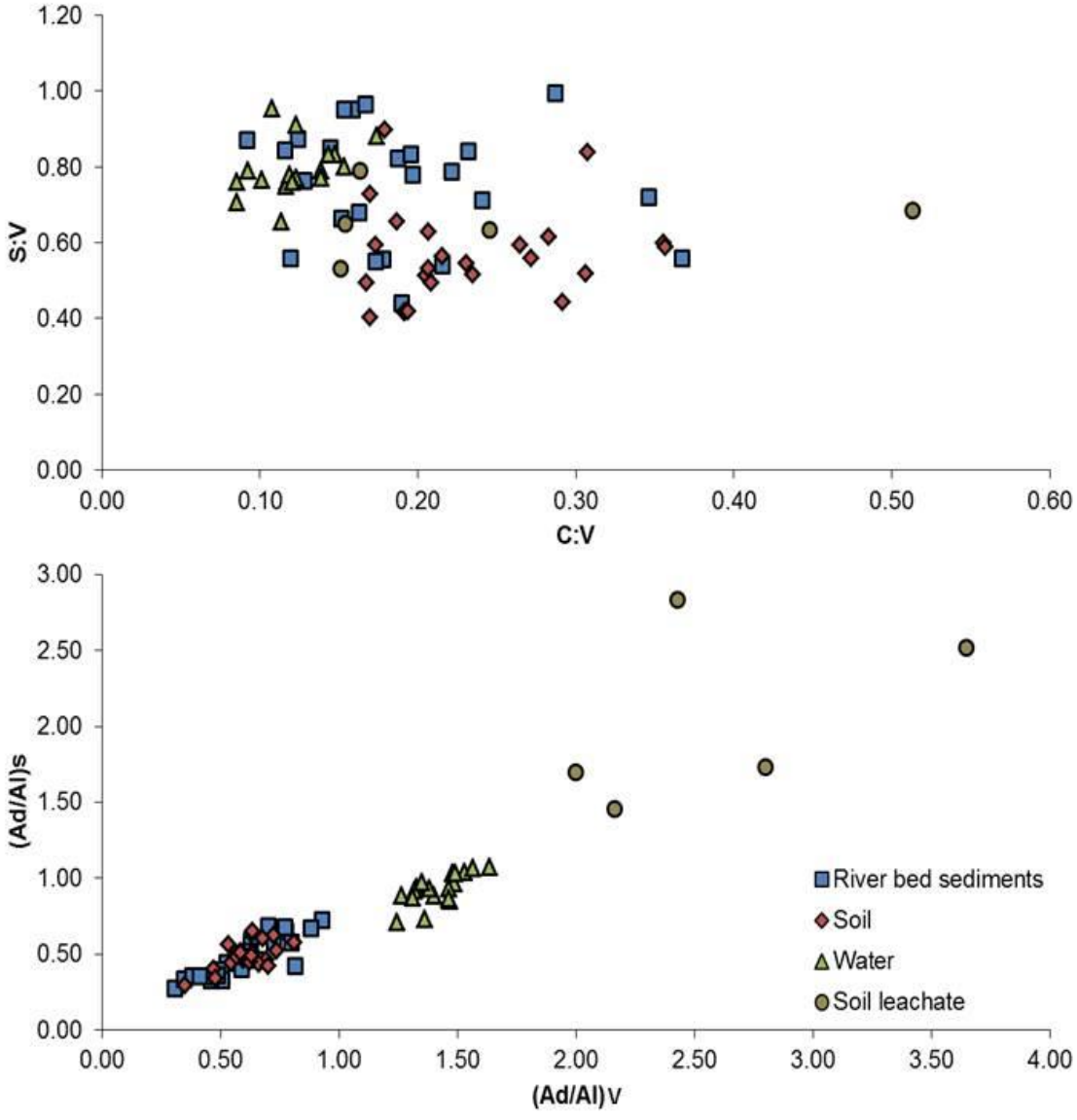

Figure 4.3: Lignin phenol ratios of vanillyl (V) to syringyl (S) and cinnamyl (C) phenols (top panel) and acid (Ad) to aldehyde (Al) ratios of S and V (lower panel) of soils, river bed sediments, river water and soil leachates in Blackwater and Tiger Creek catchments.

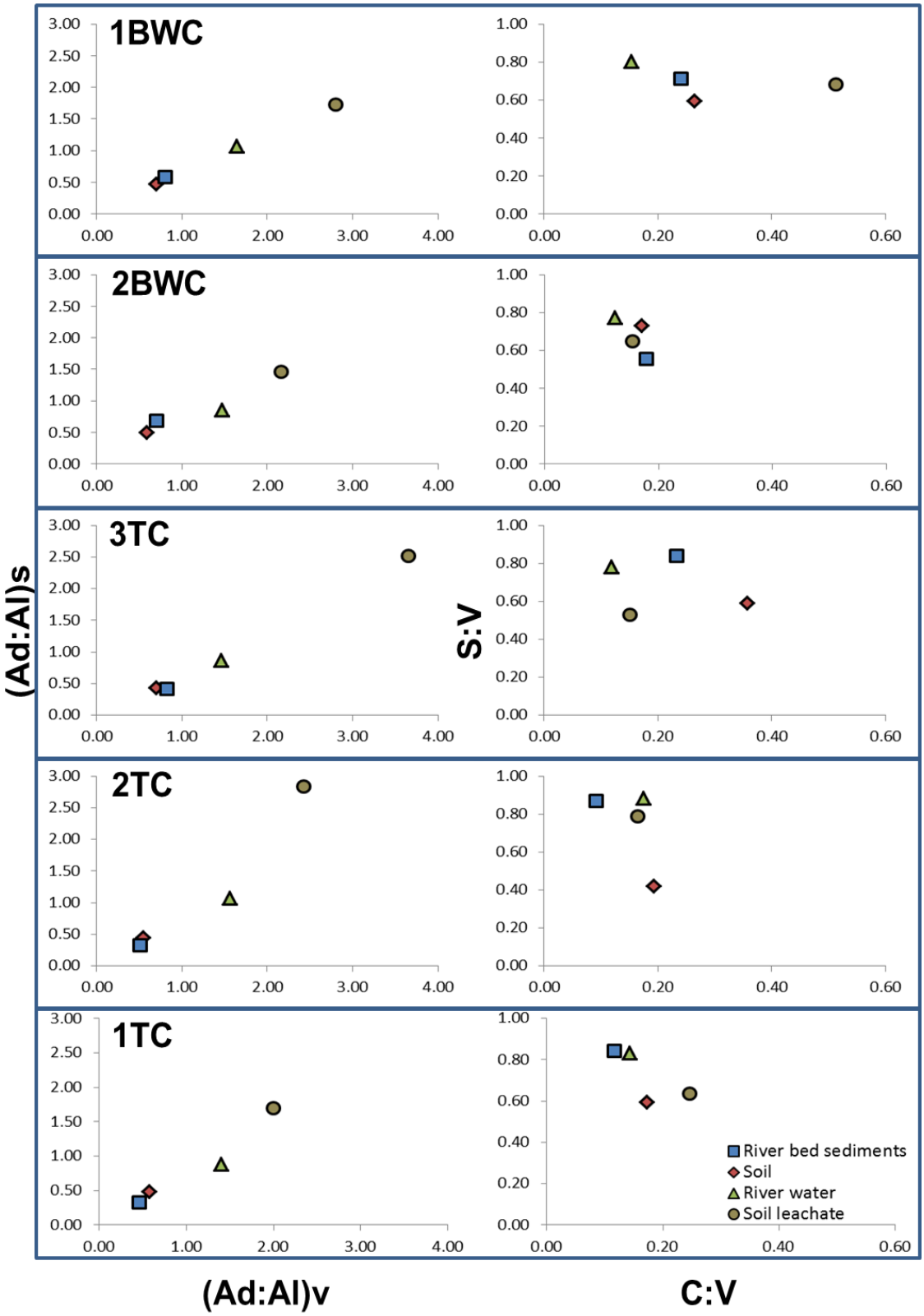

Figure 4.4: Lignin phenol ratios of vanillyl (V) to syringyl (S) and cinnamyl (C) phenols (right panel) and acid (Ad) to aldehyde (Al) ratios of S and V (left panel) of soil leachate experiments in comparison to soil, river bed sediments, river water end member ratios of lignin

Lignin Phenol ratios

The abundance of vanillyl phenols (V) relative to syringyl (S) and cinnamyl (C) phenols, allows the discrimination of angiosperm and gymnosperm sources (S:V) and non-woody and woody tissues (C:V) (Hedges and Mann, 1979). The relative abundance of lignin phenols from all soil, river bed sediments and river waters always followed the same pattern where V (43-63%) > S (25-46%) > C (4-19%) as observed previously (Aufdenkampe et al., 2007; Spencer et al., 2010b). The S:V and C:V ratios of riparian soils from the small-scale catchments were relatively constant (Table 4.1; S:V = 0.44 to 1.00 and C:V = 0.09 to 0.37). This demonstrates a mixture of vascular plant OM sources with no dominance of any of the traditionally defined angiosperm/gymnosperm and woody/non-woody end-members (Hedges and Mann, 1979), consistent with a mixed forest setting. River waters, by contrast, show a notable offset in S:V and C:V ratios compared to soils (Figure 4.3), exhibiting lower C:V and higher S:V. The S:V and C:V ratios of river bed sediments encompass the entire range observed in soils and river waters (S:V: 0.44-1.0; C:V: 0.09-0.37).

The observed S:V and C:V ratios of lignin phenols for the soils, river bed sediments and rivers are challenging to interpret without an understanding of the end member signatures resulting from underlying processes. Photochemical processes have been shown to preferentially remove coloured DOM from the river and irradiation experiments have demonstrated that whilst the C:V ratio is unaffected, the S:V ratio can increase significantly (Benner and Kaiser, 2011; Hernes and Benner, 2003; Opsahl and Benner, 1998; Spencer et al., 2009). Photo-oxidation experiments of the Mississippi and Congo Rivers, for example, found that V phenols are more susceptible to photo-degradation than S phenols with significantly increased S:V ratios (Hernes and Benner, 2003; Spencer et al., 2009). Hernes and Benner (2003) were able to further show that this increase was due to a net transfer of syringyl phenols from the high molecular weight pool (>1000 Dalton) to the low molecular weight pool (<1000 Dalton). Benner and Kaiser (2011) have also suggested that the complex molecular structure of lignin may reduce the exposure of lignin phenols to ultraviolet light thereby increasing photo-resistance.

The acid (Ad) and aldehyde (Al) ratios of V and S lignin phenols have been used to examine relative degradation states of OM, with higher ratios indicative of increased degradation (Hernes and Benner, 2003; Opsahl and Benner, 1995). The (Ad:Al)v and (Ad:Al)s of soils and sediments from the small-scale catchments clustered together and

range from 0.31 to 0.93 and 0.28 to 0.73, respectively (Figure 4.3). In contrast the (Ad:Al)v and (Ad:Al)s of DOM in the river water was significantly elevated ranging from 1.24 to 1.64 and 0.71 to 1.08, respectively (Table 4.1). This range is similar to DOM values reported for the Amazon and Congo and Rivers (Hedges et al., 2000; Spencer et al., 2012). Historically, riverine DOM has been described as highly degraded and aged due in part to the more oxidised signatures of water compared to particulate matter suggested by the (Ad:Al)v/(Ad:Al)s ratio (Hedges et al., 1997; Hedges et al., 2000). However, the apparent degraded biochemical signature of riverine DOM can also be attributed to leaching and sorption processes that have been shown to cause aqueous ratios of (Ad:Al)v and (Ad:Al)s lignin phenols to be elevated (Hernes et al., 2007). This is consistent with the results from this study, suggesting that sorption/leaching processes must be considered when interpreting the distribution of lignin parameters.

To better constrain the source signal of lignin biomarkers in our Guyanese river water samples and the possible changes in lignin composition caused by fractionation between solid and aqueous phases, water leachates of five soils were analysed (Table 4.1 and Figure 4.4). The Λ_8 results of the leachates ranged from 0.64 to 1.63 mg/100 mg OC, which is similar to the range of the respective source soils. The S:V and C:V ratios ranged from 0.53 to 0.79 and 0.15 to 0.51, respectively, and the (Ad:Al)v and (Ad:Al)s ratios ranged from 2.00 to 3.65 and 1.46 to 2.84, respectively. The S:V/C:V ratios of soil and soil leachates for each respective sample location emphasise that desorption modifies the source signal but also that there is no consistent trend across the sampling sites making the definition of appropriate end-members (i.e. soils or soil leachates) for the source signal of lignin in our river waters problematic, if not impossible. In contrast, the (Ad:Al)v and (Ad:Al)s ratios do show a strong linear relationship (R^2 = 0.93 to 0.99) between the source soil, the river water and the soil leachate. If soils and soil leachate are considered the two end-members of (Ad:Al)v and (Ad:Al)s ratios (Hernes et al, 2007), then river water DOM contains the integrated lignin signature of both (Figure 4.4). This could indicate that our desorption experiments were more aggressive or efficient in stripping OM from the soils than occurs in natural settings. We therefore propose that Guyanese river DOM has a more oxidised lignin signature compared to surrounding soil sources, which is most likely due to sorption and desorption of OM between the particulate to the dissolved phase at the terrestrial-aquatic boundary. This is consistent with other studies that highlight the partitioning between dissolved and

particulate phases is usually accompanied by fractionation of molecular components of OM due to differing solubilities and surface reactivities of OM and the mineral matrix (Aufdenkampe et al., 2001; Hernes et al., 2007; Kaiser and Guggenberger, 2000). The changing composition of lignin phenols during sorption and desorption imply that we must better constrain the source and fate end members during soil formation and river transport. Once lignin phenol end member compositions are documented for a variety of processes these important biomarkers for vascular plant material can potentially be used to understand terrestrial carbon dynamics.

Table 4.2: Down core data shown in Figure 4.2 of organic carbon (OC), nitrogen (N), $\Delta^{14}C$ and $\delta^{13}C$ of soils collected from six sites at Blackwater (BWC) and Tiger (TC) catchments in July 2010

Site	Depth	OC	N	Radiocarbon ($\Delta^{14}C$)				$\delta^{13}C$ (PDB)
	(m)	(% wt.)	(% wt.)	% modern	(+/- 1σ)	(years BP)	(+/- 1σ)	(+/- 0. 1‰)
1 BWC	0.1	0.46	0.0315	102.37	0.47	-	-	-29
1 BWC	0.4	0.06	0.024	98.99	0.45	23	37	-27.8
1 BWC	1	0.07	0.0095	109.44	0.5	-	-	-28.8
2 BWC	0.1	5.42	0.311	108.28	0.5	-	-	-29.4
2 BWC	0.6	0.39	0.0345	107.2	0.47	-	-	-28.5
2 BWC	1	0.64	0.041	107.36	0.5	-	-	-28.8
3 BWC	0.1	1.68	0.125	93.99	0.43	440	37	-26.5
3 BWC	0.6	1.74	0.1435	94.92	0.44	360	37	-26.5
3 BWC	1	1.94	0.141	85.5	0.39	1200	37	-24.7
1 TC	0.1	1.78	0.1145	105.33	0.48	-	-	-28.1
1 TC	0.5	1.57	0.131	104.98	0.48	-	-	-27.7
1 TC	1	0.87	0.0805	95.81	0.44	286	37	-26.9
2 TC	0.1	1.30	0.085	106.35	0.49	-	-	-29.5
2 TC	0.5	0.88	0.064	102.63	0.48	-	-	-29.2
2 TC	1	1.21	0.0645	92.65	0.43	555	37	-28.7
3 TC	0.1	1.54	0.0915	109.63	0.5	-	-	-28.7
3 TC	0.5	0.37	0.025	109.11	0.48	-	-	-28.9
3 TC	1	0.31	0.0305	107.2	0.47	-	-	-28.8

4.3.3 *The age of organic matter in lowland rainforests of Guyana*

A number of recent studies have shown that riverine DOM is relatively young and abundant in lignin (Mayorga et al., 2005; Spencer et al., 2012), suggesting a large contribution of fresh material that is rapidly turned over to CO_2. The $\Delta^{14}C$ signature of bulk riverine DOC in central Guyana is young ($\Delta^{14}C$-DOC ranged 106.82 to 111.02% modern; Table 4.1) as is the OM in surrounding surface soils and river bed sediments ($\Delta^{14}C$ ages range 93.99 to 109.85% modern). These data confirm that a large proportion of the OM in the Blackwater and Tiger Creek headwaters is recycled post-bomb, i.e.,

within ~60 years (Table 4.1), consistent with evidence from the Amazon (Mayorga et al., 2005). However, there are five notable exceptions in the deeper Guyanese soils where OM is older than 286 years BP. The $\Delta^{14}C$ signatures show that soil OM in wetland areas of both creeks (1 TC, 2TC and 3BWC) with similar soil carbon concentrations throughout the soil profile is significantly older than surface materials ranging from 286-1200 years BP (+/- 37 years; 95.81 to 85.5% modern; Table 4.2). These signatures argue for a higher storage potential of carbon at depth, probably due to the water-saturated nature of these wetland settings where changes in the redox conditions and potential microbial degradation pathways (i.e. from an aerobic to anaerobic environment) enhance OM preservation (e.g. Aller, 1994; Lehmann et al., 2002).

The $\delta^{13}C$ values of surface soils and river bed sediments range from -26.38 to -31.98 ‰ confirming that a majority of carbon is fixed through the C_3 pathway, as expected given the rainforest setting (Table 4.1). The $\delta^{13}C$-DOC of river water and deeper soils is much more variable, ranging from -20.33 to -30.32‰ (Table 4.2). We suggest that the low riverine carbon-normalized lignin yields (Λ_8) in conjunction with modern $\Delta^{14}C$-DOC and more enriched $\delta^{13}C$-DOC values point to a large fraction of autochthonous DOM, possibly derived from aquatic algae and/or microorganisms. Alternatively, and potentially more likely, given that $\delta^{13}C$ values observed in deeper soils become more enriched as they get older (up to ~4‰; Figure 4.2), it is also possible that the observed $\delta^{13}C$ isotopic shift of riverine DOM represents supply of OM to the river from deeper soils either from (1) remaining OM not sorbed onto the mineral phase, or from (2) an aqueous OM pool where biodegradation has largely removed bioavailable components within the total OM pool (Wynn, 2007).

4.4 Conclusion

A study of OM cycling across the terrestrial-aquatic interface of two headwater river catchments in the Guyanese rainforest show that there are large amounts of vascular plant material delivered to small-scale headwater catchments with the potential to accumulate in river bed sediments. Increases in riverine DOC and C soil storage further downstream were observed in the harvested catchment compared to the control catchment suggesting RIL may have mobilised more carbon in the form of coarse woody debris (Feldpausch et al., 2005; Olander et al., 2005). Bulk radiocarbon ($\Delta^{14}C$) measurements of riverine DOM and OM in river bed sediments show that the majority of carbon is relatively young and turned over within 60 years. Surrounding surface soils display similar ages; however, deeper soils from water saturated wetlands show a clear

potential for longer-term carbon storage with ages up to 1200 years BP. Stable isotopes of carbon confirm that a majority of OM is fixed by the C_3 pathway with the most enriched $\delta^{13}C$ signatures in soils occurring with age. We suggest that the observed isotopic fractionation between surface and deep soils is likely the result of either biodegradation of relatively labile compounds within the total OM pool or by preferential retention of isotopically enriched OM compounds by the soil matrix. Experimental data investigating the partitioning of OM between solid (soil) and aqueous phases (water) show that ratios of S:V/C:V lignin phenol biomarkers are susceptible to non-systematic change, which currently makes understanding the shift in S:V and C:V ratios of our soils, river bed sediments and river waters difficult, if not impossible. In contrast, the (Ad:Al)v/(Ad:Al)s of soil leachates always appear more oxidised than their source soils, and suggests that more oxidised forms of lignin are preferentially transported in the dissolved phase. The changes of $\delta^{13}C$ and lignin-phenol signatures observed across the terrestrial-aquatic boundary reemphasise the necessity to identify suitable end-members and their variability for these commonly used environment biomarkers. This is particular importance when investigating the effects of land use change on various storage, transport and degradation processes of carbon cycling.

Chapter 5: Mobilization of optically invisible organic carbon during a rain event from a tropical headwater river

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Abstract

We present sub-hourly geochemical records from a tropical rainforest headwater catchment in Guyana showing variable dissolved organic carbon concentration, increasing an order of magnitude (10.6 to 114 mg/L) over 13.5 hours. This exceeds the range observed during peak dry and wet seasons recorded in 2010 and 2011 (15-28 mg/L). The DOC that is mobilized and transported during wet seasons and rain events consists of non-coloured, optically invisible dissolved organic matter (iDOM) that accounts for 14-89% of the total pool and is not amenable to UV-VIS absorbance analytical techniques. The highest proportions of these bioavailable compounds correspond to maximum DOC concentrations during storm events and likely sourced from fresh terrestrial organic matter. iDOM is observed further downstream and represents a possible source of riverine CO_2 outgassing, requiring further investigation to determine its role in the global terrestrial carbon cycle.

5.1 Introduction

Inland water processes are fundamental to wider interactions between the land and ocean that directly impact global carbon and nutrient balances (Aufdenkampe et al., 2011). Global river networks annually receive an estimated 2.9 Pg of carbon (C) from the terrestrial environment but only deliver 0.9 Pg of C to the world's oceans (Tranvik et al., 2009). Consequently, rivers are now considered "active pipes" that store C in river bed sediments and recycle C to the atmosphere as carbon dioxide (CO_2;Battin et al., 2008; Cole et al., 2007). Tropical rivers alone are estimated to transport 0.53 Pg of carbon to the ocean (Huang et al., 2012) and release 0.9 Pg of carbon dioxide to the atmosphere (Richey et al., 2002). However, these estimates need to be verified as relatively few tropical rivers have been studied with small, low-latitude river systems greatly under sampled (Eglinton and Repeta, 2003). Where data is available in these regions, the focus is usually on the main channel or tidal limit of the big rivers such as the Amazon, Orinoco or Congo (Battin, 1998; Richey et al., 1990; Spencer et al., 2012). This approach is highly effective at integrating the biological and chemical signatures of the wider catchment over time but at the cost of poorly understanding the changing dynamics between upper headwaters and their larger, downstream counterparts. This is particularly evident in the tropics where small headwater rivers draining rainforest contain large amounts of dissolved organic carbon (DOC; e.g. Johnson et al., 2006b; Mayorga et al., 2005; Waterloo et al., 2006) and are highly saturated in CO_2 compared to downstream rivers (Richey et al., 2002).

Globally, small headwater catchments typically account for 70-80% of the river network (Gomi et al., 2002). It is at this small headwater scale where the impact of soil, vegetation and land use is strongest, directly linking dynamic hydrological and climatic processes with the mobilization and cycling of carbon and nutrients in the river (e.g. Dalzell et al., 2007). Tropical forests are possibly the most biologically active zones on Earth accounting for ~40% terrestrial net primary production (Townsend et al., 2011) and 17–25% of the carbon in the terrestrial biosphere (Bonan, 2008). However, limited knowledge of the temporal and spatial variability of carbon cycling at the small-scale and its underlying mechanisms limit our understanding of how changes in climate and land use affect tropical forest ecosystems as carbon sinks or sources (Wohl et al., 2012). It is therefore critical to determine the quantity, composition and potential bioavailability of riverine organic matter (OM), comprising of carbon, nitrogen and phosphorous and other elements. This study presents field and laboratory data

documenting DOC and DOM (dissolved organic matter) variability during a rain event from a pristine tropical rainforest headwater system against the seasonal background in central Guyana (Figure 5.1).

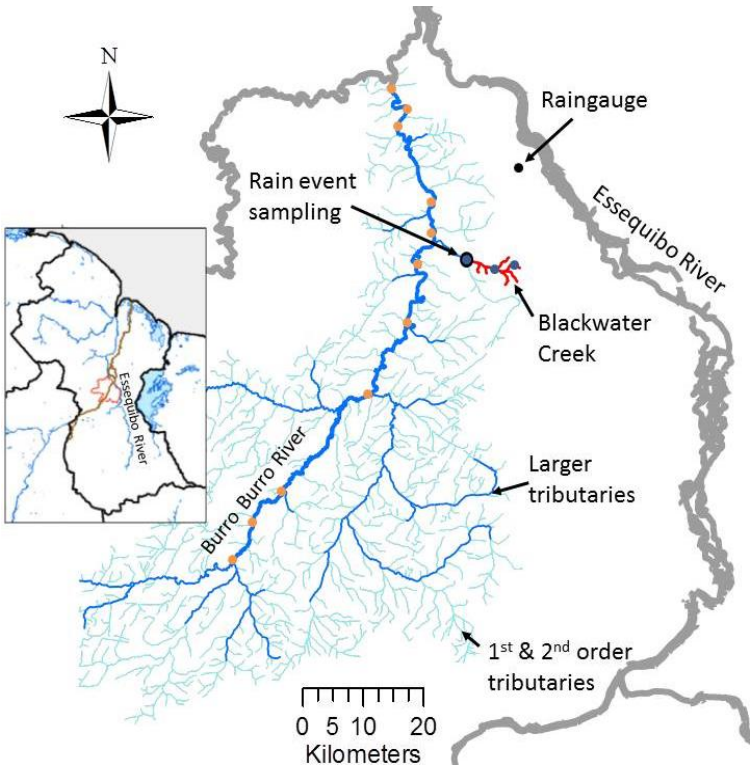

Figure 5.1: The Burro Burro catchment bounded by the Essequibo River and its tributaries to the north, east and west (in grey). Blackwater Creek is highlighted in red, the Burro Burro River is shown as a thick blue line, and waters classified as first and second order within Iwokrama are shown in turquoise. Orange dots are sampling locations from the Burro Burro River survey in March and July 2010. Blue dots are sampling locations from Blackwater Creek during March and June/July of 2010 and 2011.

5.2 Materials and Methods

In 2010 a field sampling programme was undertaken to investigate the seasonal variability of DOC concentration and composition of the Burro Burro River, a 3200 km^2 headwater catchment situated in lowland tropical rainforest of central Guyana (Figure 5.1). Water samples were collected along the main channel from the source to the confluence of the river at 24 locations during the peak dry and wet seasons (March and July). To investigate the DOC seasonal variability at the small-scale, a tributary of the Burro Burro River, Blackwater Creek (~20 km^2 catchment; Figure 5.1), was sampled from the river source downstream at three locations approximately 1.5 kms apart, forming a ~5 km transect. Three samples were collected from Blackwater Creek during March and July of 2010 and 2011(n = 12). To ascertain the role of rain events in riverine DOC transport, river water samples (~6 L) from Blackwater Creek were collected from the main channel (Figure 5.1). In total, 24 samples were collected over 13.5 hours on the 7th July 2011 during the peak wet season. All samples were field filtered (0.45 µm Pall SUPOR Acrodisc), measured for spectral absorbance (200-800 nm) using a WPA II Lightwave UV-Vis spectrophotometer (Biochrom) and subsequently kept frozen in Nalgene bottles in the dark. Water samples were analysed in the laboratory for DOC, δ^{13}C-DOC, size exclusion chromatography (SEC), lignin

phenol biomarkers, $\delta^{18}O$ and $\delta^{2}H$. For a full description of the analytical methods used see section 2.3.

5.3 Results and Discussion

Globally, the concentration of DOC in most river waters has a strong relationship with colorimetric dissolved organic matter (CDOM) from humic substances (Weishaar et al., 2003). When calibrated for an individual river, UV-visible absorbance can be used as a robust proxy to provide high-resolution DOC concentration time-series, through direct sampling (Spencer et al., 2012), in-situ probes (Jeong et al., 2012), or remote sensing (Griffin et al., 2011). This strong correlation between DOC concentration and UV-visible absorbance has been seen in river systems across all climate zones, including some limited studies of tropical rivers (Spencer et al., 2010b; Yamashita et al., 2010). We also observe this relationship in the Burro Burro River during the dry season but not in the wet season of 2010 (Figure 5.2 data shown in Table 5.1). Using UV absorbance at 254nm (UV_{254} after Weishaar et al. (2003)) we observe a linear correlation (R^2) of 0.85 in the dry season (DOC = 6-19 mg/L; UV_{254} = 0.13-0.68) but only 0.04 in the wet season (DOC = 12-27 mg/L; UV_{254} = 0.18-0.70). This decoupling between UV_{254} and DOC concentration was also observed at other commonly used wavelengths (300, 270, 350 and 440nm) and suggests that during the wet season the river is transporting OM that is largely non-coloured, non-humic and optically invisible to UV absorbance spectroscopy. We therefore define the term "invisible" DOM ("iDOM") as the non-coloured component of the total riverine DOM pool.

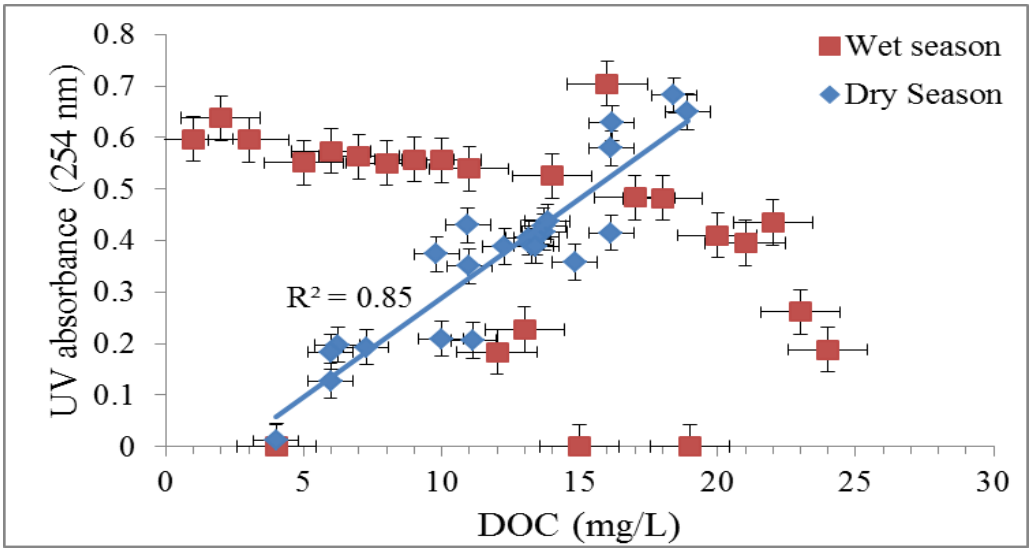

Figure 5.2: DOC and UV absorbance (UV_{254}) scatterplots of water collected from 24 locations across the Burro Burro River (note some points are obscured) in 2010 from the dry season (March; blue) and wet season (July; red).

Table 5.1: DOC and UV absorbance (UV_{254}, UV_{270}, UV_{350}, UV_{350}) of water collected from 24 locations across the Burro Burro River in 2010 from the dry season (March) and wet season (July).

Sample site	Dry season (March 2010)				Wet season (July 2010)			
	UV_{254}	UV_{270}	UV_{350}	DOC (mg/L)	UV_{254}	UV_{270}	UV_{350}	DOC (mg/L)
1	0.405	0.354	0.127	13.16	0.597	0.526	0.191	18.28
2	0.011	0.009	0.002	4.01	0.638	0.563	0.208	14.05
3	0.416	0.364	0.131	13.71	0.595	0.524	0.196	12.17
4	0.628	0.555	0.197	16.17	-	-	-	-
5	0.388	0.340	0.120	12.29	0.551	0.485	0.177	17.98
6	0.390	0.345	0.123	13.25	0.573	0.504	0.186	13.92
7	0.650	0.574	0.207	18.90	0.563	0.495	0.180	16.79
8	0.428	0.376	0.135	13.69	0.550	0.482	0.177	13.67
9	0.579	0.510	0.185	16.14	0.557	0.490	0.178	19.45
10	0.415	0.363	0.129	16.15	0.556	0.488	0.179	24.25
11	0.406	0.356	0.127	13.43	0.539	0.474	0.176	27.27
12	0.430	0.378	0.137	10.94	0.183	0.161	0.061	13.39
13	0.437	0.384	0.140	13.83	0.227	0.201	0.080	15.44
14	0.389	0.343	0.126	13.43	0.525	0.459	0.167	17.98
15	0.682	0.602	0.223	18.42	-	-	-	-
16	0.373	0.329	0.121	9.82	0.704	0.619	0.225	21.33
17	0.358	0.317	0.118	14.83	0.483	0.421	0.152	13.11
18	0.127	0.112	0.041	5.97	0.482	0.420	0.150	16.38
19	0.350	0.309	0.113	11.01	-	-	-	-
20	0.206	0.181	0.065	11.14	0.410	0.359	0.132	12.07
21	0.209	0.184	0.065	9.99	0.395	0.347	0.127	16.57
22	0.197	0.174	0.063	6.23	0.435	0.381	0.141	12.97
23	0.183	0.162	0.058	5.99	0.261	0.234	0.101	12.94
24	0.193	0.168	0.060	7.27	0.188	0.168	0.067	19.05

In the Burro Burro catchment, ~70% of the land area is drained by first and second order tributaries (Figure 5.1). Therefore, the decoupling of CDOM and DOC during the wet season, Blackwater Creek (a second order tributary) was investigated to determine whether small-scale headwaters more widely supply iDOM downstream to the larger Burro Burro River. A hydrological record of Blackwater Creek (from March 2010 to August 2011) shows a strong response in the flow and a potential influence of the OM supply to the river during short rain events (Figure 5.3). Therefore, during the peak wet season of 2011, a detailed field study was undertaken, sampling the river at a half-hour resolution for 13.5 hours over the course of a rain event.

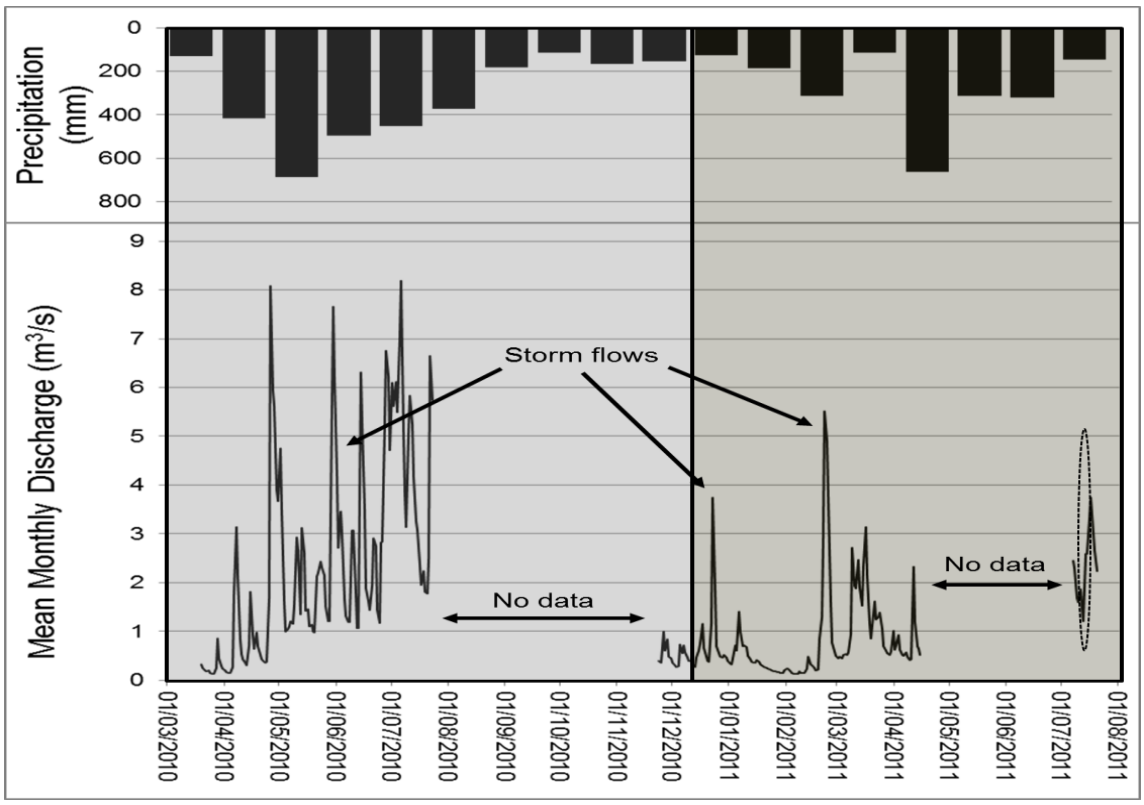

***Figure 5.3**: The time-series of Blackwater Creek discharge and monthly precipitation from March 2010 to August 2011. Black circled area indicates time of rain event sampling however the data logger did not record the event accurately.*

Our 13.5 hour time-series from Blackwater Creek reveal an order of magnitude increase in DOC (10.6 to 114.0 mg/L), by far exceeding the range observed during peak dry and wet seasons recorded from the Burro Burro River and Blackwater Creek in 2010 and 2011 (15-28 mg/L; Table 4.1). This peak in DOC is also outside of the ranges reported for Amazonian headwaters during storm events (Johnson et al., 2006b; Waterloo et al., 2006) but within the range observed from overland flow in Canadian forest systems (Hinton et al., 1998). This left these authors to speculate that overland flow could supply significant amounts of DOC to the river if the water volume was great enough. In the Canadian forest, however, this signal was not recorded in the headwater itself and therefore may not be directly comparable to our observations from the Guyana headwater rivers. The stable water isotopes of Blackwater Creek, used as tracers of changes in catchment hydrology, displayed little variation during the sampled rain event (Table 5.2; $\delta^{18}O$ = -5.3 and $\delta^{2}H$ = -27.0 to -26.4‰) suggesting that there was little or no change in the hydrology flow path during the observation period. Nevertheless, we anticipate that any change in flow path would not be captured in the oxygen and hydrogen stable water isotopes if the catchment was significantly saturated by recent precipitation. Our short time-series shows that riverine DOC dynamics operate very

differently during high river discharge (rain events), when compared to lower flows. This highlights the importance of short-term (hourly to sub-hourly) interactions between hydrology, vegetation, soil mineralogy and river geochemistry as controls of carbon transport and cycling. Concomitant with fluctuations in DOC, the carbon sources are also highly dynamic throughout the time-series. The $\delta^{13}C_{DOC}$ values range from -22.0‰ at low DOC concentrations to -30.3‰ at high DOC (Figure 5.4). The significantly more negative $\delta^{13}C$ signatures during high DOC may indicate preferential supply from terrestrial C_3 vegetation of surrounding soils (measured range of -26.5 to -31.1‰ 0-1m below ground, data not shown). No C_4 vegetation occurs in the catchment and it is also unlikely that there is sufficient autochthonous material (e.g. microbial or macrophytic) to cause $\delta^{13}C$ enrichment due to the short residence time in these small-scale headwaters. Alternatively, the shift in $\delta^{13}C$ may represent changes in the composition of the total OM pool from biodegradation processes either at the surface or during transport to the subsurface, where bulk signatures of degraded OM can be enriched by up to 6‰ compared to "fresh" OM (e.g. Wynn, 2007). Further work, including isotopic and compound-specific approaches are required to establish end member signatures and biogeochemical mechanisms of carbon isotope fractionation during the decomposition of OM within Guyanese and other rainforest.

Notably, UV-visible absorbance data from our rain event time-series in Blackwater Creek do not respond to changes in DOC (R^2 = 0.01), consistent with the larger scale observations from the Burro Burro River. Lignin phenol biomarker data (Σ_8; Figure 5.4), however, confirm that vascular plant (humic) material is present throughout the time series. Possible other interference by elements, in particular iron (Table 5.2; Fe = 0.21-0.40 mg/L) masking the UV signature, do not explain the UV-visible absorbance results as the pH (4-5) and redox (pe = 4.1-4.8) conditions favour free Fe^{2+}. The latter has been shown to have minimal interference with UV absorbance at 254nm (Doane and Horwath, 2010). Interestingly, the Fe concentrations follow a similar pattern as the electric conductivity measurements throughout the time-series (Table 5.2). This suggests that whilst the rain event mobilised carbon to the river it did not have a large effect on conductive species such as trace metals that could be an indicator of mineral supply to the river.

Table 5.2: Hydrological/geochemical time-series of river water from a small-scale headwater (Blackwater Creek) encompassing a rain event (07/07/2011).

Time	River	Precip-	OC	Fe	Field Measurements			River water isotopes			SEC Composition			Lignin	UV-VIS Absorbance			
Elapsed	Discharge	itation	<0.45µm		Cond.	pe	pH	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C$ DOC	Humics	iDOM	Other	Σ8	a_{254}	a_{270}	a_{350}	a_{700}
(mins)	(m^3/s)	(mm)	(mg/L)		(µS/cm)			(‰ VSMOW)		(‰ PDB)		(%)		(µg/L)	nm (cm^{-1})			
0		0.0	19.68	0.40	16.98	3.07	5.33	-5.3	-27.0	-24.8	64	34	2		0.69	0.61	0.26	0.016
45	1.40	0.0	26.01	0.41	16.88	3.23	5.92			-23.6	82	15	3	85.35	0.72	0.64	0.28	0.024
75	2.09	0.0	39.91	0.38	17.37	3.49	5.23			-22.0	48	47	5	63.49	0.70	0.62	0.27	0.021
105	1.19	2.5	31.99	0.34	16.83	3.96	4.84			-24.8	49	49	2		0.69	0.62	0.27	0.023
240	2.47	2.5	11.36	0.37	16.86	4.17	4.62			-22.9	77	21	2	82.45	0.70	0.63	0.27	0.022
270	2.39	30.5	10.64	0.39	16.81	4.40	4.45	-5.3	-26.8	-25.5	75	23	2	72.74	0.69	0.61	0.27	0.021
300	1.57	2.0	35.25	0.39	16.82	4.45	4.45			-22.9	34	64	2	85.31	0.69	0.62	0.27	0.022
330	1.85	0.5	21.47	0.38	16.77	4.66	4.37			-25.7	61	38	1		0.69	0.62	0.27	0.021
360	1.66	0.0	10.97	0.39	16.84	4.59	4.38	-5.3	-26.6	-26.8	75	23	2	65.13	0.72	0.65	0.29	0.032
390	1.16	1.0	11.89	0.39	16.78	4.61	4.40			-25.7	78	17	5		0.68	0.61	0.26	0.019
420	2.82	0.5	28.79	0.40	17.13	4.67	4.37			-24.6	81	17	2	78.59	0.67	0.60	0.26	0.014
450	2.89	0.5	34.06	0.40	16.89	4.66	4.42			-25.0	30	70	1		0.67	0.60	0.26	0.018
480	3.00	0.0	24.83	0.40	16.91	4.69	4.41	-5.3	-26.6	-25.4	57	42	1	73.23	0.68	0.60	0.26	0.015
510	2.98	0.0	51.02	0.39	16.78	4.72	4.41			-26.9	23	76	1	56.31	0.67	0.60	0.26	0.015
540	2.97	0.0	29.14	0.37	16.77	4.71	4.40			-27.8	42	57	1	78.01	0.70	0.63	0.28	0.023
570	2.81	0.0	114.0	0.21	16.80	4.81	4.38	-5.3	-26.5	-29.4	13	84	3	77.13	0.68	0.61	0.27	0.019
600	2.95	0.0	100.9	0.29	16.78	4.84	4.38			-30.3	10	89	0		0.72	0.64	0.29	0.029
630	2.87	0.0	85.62	0.40	16.84	4.84	4.38			-26.9	14	81	4		0.68	0.60	0.26	0.014
660	2.82	0.0	64.50	0.39	16.83	4.86	4.38	-5.3	-26.4	-27.1				84.18	0.68	0.60	0.26	0.016
690	2.71	0.0	11.61	0.21	16.76	4.86	4.39			-24.6	84	14	2		0.67	0.60	0.25	0.012
720	2.15	0.0	12.94	0.40	16.91	4.83	4.41			-23.8	79	19	2	68.63	0.68	0.61	0.26	0.020
750	2.36	0.0	35.19	0.40	16.84	4.89	4.41			-23.2	30	69	1		0.71	0.64	0.28	0.026
780	2.66	0.0	66.51	0.34	16.60	4.89	4.42			-26.0	23	77	1	61.87	0.72	0.64	0.29	0.027
810	2.59	0.0	74.68	0.38	16.78	4.91	4.39			-27.0				79.60	0.71	0.63	0.28	0.027

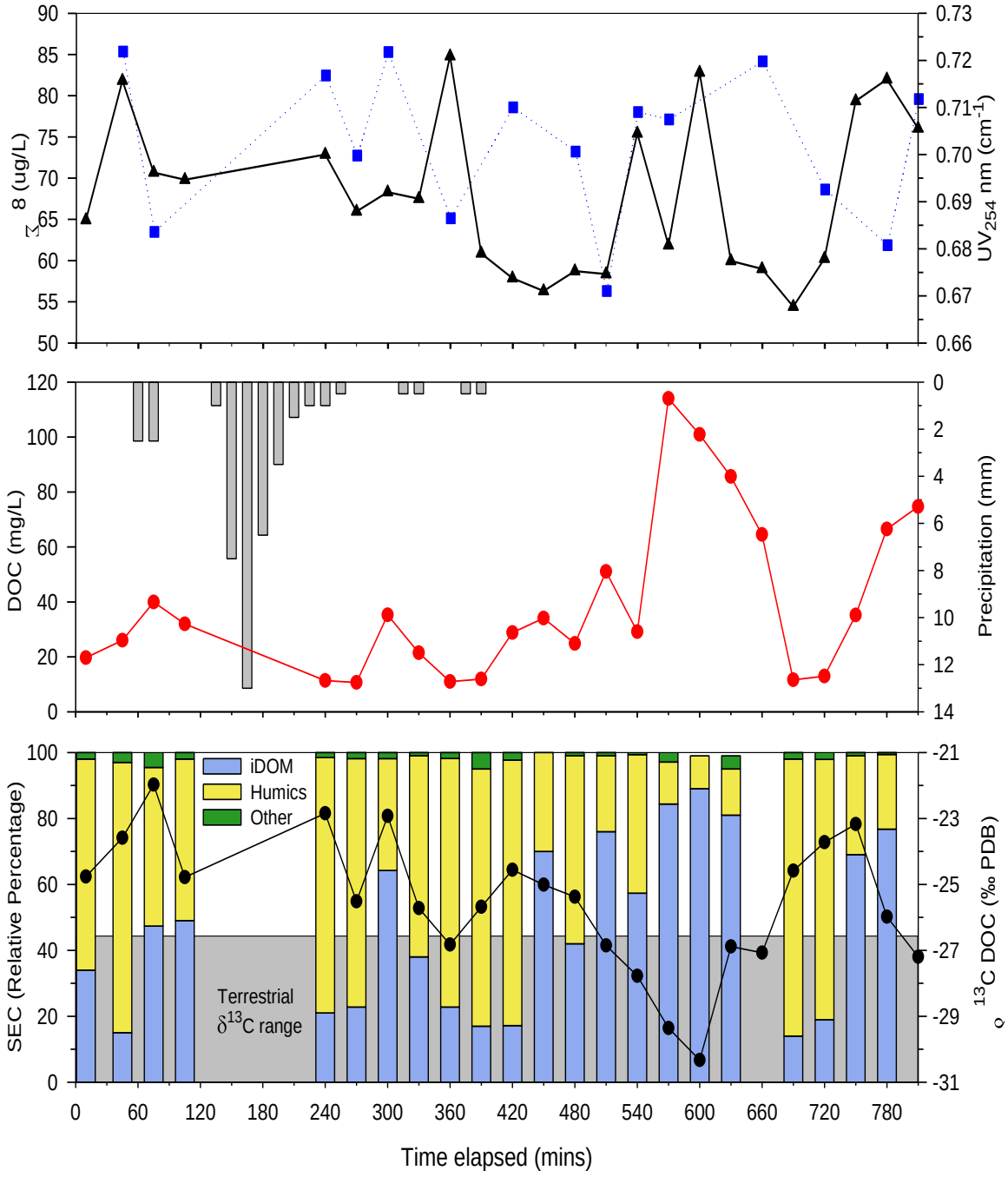

Figure 5.4: Data collected from Blackwater Creek over 13.5 hours encompassing a rain event. Upper panel shows UV absorbance measured at 254 nm (black line and triangles) and lignin phenol oxidation products (Σ8; blue dashed line with square markers). The middle panel shows measured DOC (red solid line and circles) and precipitation measured nearby (~15 km). Lower panel shows the SEC derived DOM composition as relative percentage bar of humic organic matter (yellow), iDOM (blue) and other minor compounds (green). The black line is $\delta^{13}C$ of DOC with the grey box displaying the $\delta^{13}C$ range observed in local forest soils indicating a predominantly terrestrial C_3 carbon fixation pathway.

The composition of the total riverine DOM pool during the 13.5 hour time-series was further explored using SEC, which demonstrates that humic substances and iDOM are the two most significant components of DOM. Importantly, the iDOM fraction contributes between 14 and 89% to the total DOM pool, with the highest fractions

occurring during maximum DOC and most depleted δ^{13}C-DOC (Figure 5.4). iDOM is likely bioavailable, comprising of carbohydrate degradation products such as of mono- and oligosaccharides, alcohols, aldehydes, ketones and amino sugars (Huber et al., 2011) that originate from terrestrial plant OM sources. The contribution of iDOM identified by SEC is surprising when compared to results from DOCSpec model output (Carter et al., 2012), which has been shown to accurately predict DOC concentrations of nearly 1700 rivers with a non-absorbing carbon (iDOM) constant of 0.8 mg/L was assumed. Therefore, as the DOCSpec model dataset is based on temperate and boreal river catchments and high order tropical rivers, our results imply that tropical headwater rivers may mobilise and transport significantly more non-UV absorbing DOM than their mid and high latitude equivalents, possibly related to short but heavy rain events.

One possible hypothesis explaining the change in DOM composition in the Guyana headwater catchments is a change in the hydrological pathway, mobilising different OM pools from either the surface or the shallow subsurface with changing hydrological conditions. During rain events and wet periods, high intensity surface runoff and shallow subsurface flow has been shown to dominate across the tropics (Elsenbeer, 2001; Johnson et al., 2006a). This would mobilise large amounts of fresh terrestrial OM that contains a significant proportion of iDOM consistent with the evidence presented in this study (Figure 5.4). In contrast, during drier periods water percolates deeper through the soil profile transporting OM to the subsurface. This slower process (compared to surface and overland flow) would allow OM-mineral interaction to occur and change the relative abundance of iDOM to the total OM pool that is leached out to the river (Kaiser et al., 2004; Kalbitz et al., 2005). As a consequence, the dry season OM pool becomes relatively enriched in humic compounds, which are flushed out during base flow leading to a more humic (coloured) signature of DOM in the river water. The latter succession of processes would explain the decoupling observed between DOC and UV_{254} in the Burro Burro River 2010 wet season (Figure 5.3).

5.4 Conclusion

The rain event time-series presented in this study demonstrates that a substantial amount of iDOM is mobilized in Guyanese headwater rivers and probably represents an intermediate group of bioavailable substances in a state of flux that can be transported further downstream. This emphasizes the importance of the terrestrial-aquatic interface of small-scale tropical headwater rivers as hotspots and hot moments of biogeochemical cycling (McClain et al., 2003). The fate of iDOM is currently unknown but we suggest

that given the bioavailability of iDOM, its degradation in the river could provide a substantial contribution to CO_2 outgassing at the small river scale (Mayorga et al., 2005; Richey et al., 2002), adding to the much better documented and quantified outgassing from riverine DIC and deep soil root systems (Davidson et al., 2010; Richey et al., 2002). Further research is required to assess the quantitative significance of iDOM sourced from small tropical rivers and the role of microbial communities in utilizing iDOM and its degradation products within the soil and the river. As such, detailed spatial and temporal studies from other tropical headwater river systems, not just the main downstream channel, are essential to validate and quantify the role of iDOM in the wider terrestrial carbon cycle.

Chapter 6: Research Summary and Outlook

Earth is constantly changing with a multitude of biogeochemical processes and interactions that operate across a wide continuum of spatial and temporal scales, defining the dynamic boundary conditions of the ecosphere, have to live and adapt to. By identifying "hot spots" and "hot moments" of activity for each of these scales we can determine important bioactive elements and reactions that determine the response of ecosystems to climate and land use changes (McClain et al., 2003). This project studies the extremely short moments and small spots of tropical rainforest rivers, the ultimate source region where carbon and nutrients are dynamically transferred via hydrological processes from the soils and vegetation to the river environment.

6.1 A brief review

The Earth's carbon in unevenly distributed between terrestrial, oceanic and atmospheric reservoirs (Cole et al., 2007; Falkowski et al., 2000) that are inter-connected through chemical, biological and physical pathways that operate on time-scales from seconds to millennia. The terrestrial biosphere is a key component of the Earth's carbon system providing both positive and negative feedbacks to climate change. However, the advent of the industrial age has changed the way carbon is transported between the major carbon stores by disturbing natural fluxes and creating new pathways and potential feedback mechanisms (IPCC, 2007).

Tropical forests only cover around 10% of the land surface (Lewis, 2006) and yet are one of the most important biomes on Earth, supporting ~50% of all species on the planet (Malhi and Grace, 2000), exchanging massive amounts of water and energy with the atmosphere (Fisher et al., 2009; Foley et al., 2003; Malhi et al., 2009) and storing ~17–25% of the carbon in the terrestrial biosphere (Bonan, 2008). This is reflected in the carbon export by tropical rivers which transport over half of global estimates to the world's oceans (Huang et al., 2012). With tropical ecosystems consistently under threat from changing climate and land-use (Balch et al., 2008; Brando et al., 2008; Davidson et al., 2008; Lewis et al., 2004; Nepstad et al., 2008) a major science challenge is to understand and predict ecological dynamics in tropical forests at multiple scales (Townsend et al., 2011). One key focus of research that sets the scene for this project has been to establish the timescales of "hot moments" where tropical forests cycle water and carbon and determine how the interactions of inland water bodies, particularly upper headwaters of rivers (hot spots) that typically account for 70-80% of the total

river network (Gomi et al., 2002), control the forcing and feedback of carbon and water on a global scale (Aufdenkampe et al., 2011; Bonan, 2008).

6.2 Addressing the defined research aims and hypotheses

The initial motivation for this project was to identify, characterize and quantify the hot spots and hot moments of tropical rainforest Guyana headwaters within the seasonal climate context over a two-year period from 2010-2011. The main objective was to establish the range of hydrological variability and its effect on the leaching of carbon from soils and their subsequent transport and alteration in headwaters. This has led to three scientific hypotheses to be tested in this project:

i. *The amount of organic carbon (OC) exported from riparian soils to the river in tropical headwaters catchment is linearly related to rainfall, approaching peak levels during precipitation event, and demonstrates a dry to wet seasonal pattern.*

ii. *OC is distributed in two main pools of organic matter (OM):*
    1. *low molecular weight (LMW) and labile; and*
    2. *higher molecular weight (HMW) and more refractory.*

    A large fraction of the high molecular, older OM is remineralised while travelling through headwater catchments, resulting in preferential export of low molecular OM to the larger river system.

iii. *The anthropogenic influence on the carbon cycling is amplified in reduced impact logging (RIL) areas when compared to pristine conditions and detectable with the proposed sampling and analytical approach.*

The scientific evidence for each hypothesis is present in sections 6.2.1, 6.2.2 and 6.2.3 respectively.

6.2.1 *Export of organic carbon from tropical riparian soils to the river*

Three years of data from central Guyana capture a reduced rainfall regime in 2009 and an extended wet season in 2010. This is in contrast to the longer term average and demonstrates that the study period was characterised by seasonal extremes related to anomalies in the positioning of the Inter-Tropical Convergence Zone (ITCZ) (Lewis et al., 2011; Marengo et al., 2012). The new rainfall records of this study show that modelled precipitation from satellite TRMM and ECMWF ERA-Interim reanalysis generally capture the pattern of seasonality, but substantially underestimate rainfall

amounts in the primary wet season (by up to 50% and 72% respectively) and overestimate precipitation in the dry season (ERA-Interim by up to 175%). This reemphasises the complexity of tropical climate systems and the necessity of ground-based field data to validate and calibrate remote sensing and modelling data. The isotopic chemistry of river waters for the study area show that δ^2H /$\delta^{18}O$ during the peak wet season is dominated by rapid runoff from isotopically lighter water derived from the rains of the ITCZ. These results provide evidence of the close coupling of water chemistry of headwater rivers to the positioning of the ITCZ over the region.

The data present in this thesis cannot directly test whether C export from soils to rivers is linearly related to rainfall, however, it shows the direction forward for further research. At the seasonal timescale, the main Burro Burro River in Guyana demonstrates increases in dissolved organic carbon (DOC) concentration of ~10 mg/L from the dry to the wet season of 2010. At the next smaller, headwater scale, these seasonal variation of DOC concentrations (15-28 mg/L) are dwarfed by the range of DOC concentrations observed during a single precipitation event (10-114 mg/L). This suggests that rain events in the core tropics are the 'true' hot moments of DOC supply to the river. These results also emphasise that caution must be taken when using single point riverine measurements to characterise temporally variable catchments. The riparian soils of the small-scale study catchments range from 0.48-10.35% wt. demonstrating a potential source of carbon to the river. Further research must now determine if there are significant seasonal changes in the quantity and composition of carbon within headwater soils, which is expected but difficult to ascertain in this study.

6.2.2 *Organic matter pools, molecular composition and fate*

The strongest evidence of the distribution of organic carbon between high and low molecular weight groups has been observed in riverine dissolved organic matter (DOM) throughout a rain event in the small-scale Blackwater catchment. During this 13.5 hour time-series the DOC ranged from ~10 mg/L to ~114 mg/L. The peak concentrations are characterised as largely low molecular weight (LMW), non-coloured, non-humic organic matter, described as UV "invisible" DOM that accounts for up to 89% of the total pool and exhibits a strong $\delta^{13}C$ terrestrial signature from surrounding soils (~-30.3‰). At lower DOC concentrations, the OM is characterised by a higher content of humic substances and HMW (up to 82%) with a more enriched $\delta^{13}C$ (~-22.0‰).

Bulk radiocarbon ($\Delta^{14}C$) measurements of riverine dissolved organic carbon and organic matter in surface soils and river bed sediments from Tiger and Blackwater catchments show that the majority of organic carbon is relatively young (60 years BP), as anticipated from related studies in tropical rivers (e.g. Mayorga et al., 2005; Trumbore and Barbosa de Camargo, 2009). The stable isotope ($\delta^{13}C$) signature of the young carbon confirms that a majority of OM is fixed via the C_3 pathway. Deeper soils from water saturated wetlands, however, show a clear potential for longer term carbon storage with ages up to 1200 years BP with the most enriched $\delta^{13}C$ signatures in soils occurring with age. Given that younger carbon within soils has a depleted $\delta^{13}C$ signature compared to older soil OM and that "invisible" DOM (iDOM) in Blackwater Creek also demonstrates a similar $\delta^{13}C$ signature, it is likely that iDOM is relatively less degraded than humic material (e.g. Wynn, 2007). To confirm this, compound specific isotope analyses are required to identify the end member $\delta^{13}C$ values of humic and iDOM compounds in leaf litter, soil, soil leachate and riverine DOM.

Humic substances are largely expected to contain lignin, a complex component of all vascular plants. Experimental data investigating the partitioning of OM between soils and water show that the composition of lignin phenols changes between solid and aqueous phases and that the lignin composition is highly dynamic due to OM-mineral interaction (Kaiser and Guggenberger, 2000; Kalbitz et al., 2005; Kramer et al., 2012). The latter reemphasises the necessity of identifying end member lignin ratios of in the environment to understand and quantify storage, transport and degradation processes of organic matter. Whether lignin is the OM pool responsible for older carbon observed in deeper soils remains an open question for future research, but there is initial, solid evidence from this study to support this conclusion.

6.2.3 *Anthropogenic impact on carbon cycling*

At the small scale, there are no observed differences in $\delta^{2}H$ and $\delta^{18}O$ values between Blackwater and Tiger Creek catchments, suggesting that the observable variation in the hydrological cycle from RIL practices (for example, due to evaporation changes as a result of RIL practices) do not produce detectable signals, at least not for the techniques applied. Increases in riverine DOC and C soil storage further downstream were observed in the harvested catchment compared to the control catchment suggesting RIL may have mobilised more carbon, e.g. in the form of coarse woody debris (Feldpausch et al., 2005; Olander et al., 2005). However, the spatial heterogeneity observed within

the soils and the diversity associated with mixed forest of the small-scale catchments requires a greater sampling density to confirm this initial finding. Additional data such as rainforest canopy gap analysis, biomass productivity, throughfall rates and light availability are also necessary to constrain the effects of RIL (Prescott, 2002; van Dam, 2001).

6.3 Future direction of tropical rainforest research

The new dataset from Iwokrama demonstrates that the climate dynamics of tropical rainforests are poorly characterised by global datasets. We further show that tropical rain events release large quantities of OM from soils to the river over very short time periods. This is despite $\Delta^{14}C$ data indicating that some soils are capable to retain old carbon for long periods of time. We also demonstrate that there are changes in the quantity and composition of OM transported by the main Burro Burro River between dry and wet seasons. Given the important role that tropical forests and their rivers have in global carbon and water cycles and our current inability to model or accurately monitor these processes remotely, it is essential to conduct further focussed research that targets these key weaknesses in our current understanding of underlying processes.

Achieving a wider understanding of tropical carbon dynamics at the terrestrial-aquatic boundary within the global carbon cycle requires a combination of geochemical and hydrological parameters. The evidence presented in this study clearly shows that the large heterogeneity observed within the riparian soils of the headwater catchments necessitates a higher spatial resolution to adequately characterise the changing sources and supply of OM to the river. Equally important, river water sampling must capture very rapid responses during rain events at a resolution of 30 minutes or less to ensure that compositional changes in highly dynamic DOM are detected at the full scale. Furthermore, the spatial relevance of the processes identified in small tropical headwaters relative to those in the main river need to be better constrained. This research will also demonstrate whether the patterns observed in Iwokrama are representative of other tropical rainforest catchments. If so, this will likely have significant implications on the overall carbon balance of entire river watersheds and possibly even global climate, shifting the spotlight from the main river to the thousands of small headwater streams in the tropics.

This research has made a number of interesting and arguably unexpected observations that cannot be addressed in this single study; however, they set the agenda for further research. The following questions can be extracted to be followed up in other studies:

i. *Is iDOM a generic component of tropical rivers and if so how does it vary across the different river orders?*
ii. *How is DOM mobilised from the soil and what components of the OM are preferentially stored (OM-mineral interactions)?*
iii. *What is the net effect of microbial and photochemical oxidation on DOM recycling during riverine transport?*
iv. *What is the contribution and variability of this mineralised DOM to total riverine CO_2 outgassing and nutrient supply?*
v. *Once better quantified, how important is this DOM for the river carbon balance, global climate, and riverine ecosystems?*

To address the overarching questions, four hypotheses need to be tested:

i. *Leachates from surface litters and soils contain much higher proportions of labile material (iDOM) than leachates from deeper soils. Therefore the highly variable composition of tropical riverine OM over short timescales is a direct response to hydrological events (rain storms) that favours different pathways of OM transport. These pathways can be traced across a range of increasing order of streams of tropical headwater catchments.*
ii. *The lateral transport of OM is dominated by wet season storm events with coloured DOM (CDOM) strongly relating to degraded complex macro-molecule plant derived lignin material (e.g. Helms et al., 2008; Weishaar et al., 2003), whereas the difference between CDOM and total DOC represents fresh, labile and low molecular cellulosic plant material that provide essential nutrients for river ecosystems via microbial processing*
iii. *The Guyanese headwaters are areas of intense biogeochemical activity (hot spots) which process large amounts of labile OM (iDOM). The mineralisation, either microbial or photochemical, of iDOM releases CO_2 from the river adding to CO_2 from other pools (including soil and riverine dissolved inorganic carbon).*
iv. *Small river catchments elsewhere in tropical rainforest behave similarly to those in Guyana.*

It is essential for future studies investigating the carbon dynamics of inland tropical waters to consider all forms of carbon (dissolved and particulate fluxes of organic and inorganic carbon) and its interaction with the local hydrology. Only by using this comprehensive approach will our understanding of carbon cycling be improved. As such, a comprehensive geochemical approach is required that places biomarkers diagnostic of specific process and compound groups (e.g. iDOM) in the context of the much larger bulk OM pool. This fundamental challenge requires a nested analytic approach that utilises the entire suite of in-situ geochemical measurements (pH, oxidation reduction potential, electrical conductivity and CDOM), hydrological field measurements (rainfall, evapotranspiration, groundwater and surface water), subsequent advanced geochemical characterization of the various OM pools in specialist laboratories, and computer modelling. In combination, this would provide first quantification of total OM pools and initial insight into the contribution of iDOM compounds.

Laboratory work should aim to identify the relative contribution of different OM pool. Compound group-specific analyses are particularly useful with size exclusion chromatography (SEC) able to separate aqueous DOM into fractions including humic substances, iDOM (comprising mono- and oligosaccharides, alcohols, aldehydes, ketones and amino sugars) and biopolymers (polysaccharides, amino sugars, polypeptides, proteins). It is also powerful in quantifying the contribution of humic, UV-absorbing material vs. degraded carbohydrate products that are not UV-absorbing. To complement the aqueous compound group specific analyses, the relative contribution of organic fractions with different levels of reactivity in solid samples (i.e. hemi cellulose-like, cellulose-like and lignin-like substances in soils and river bed sediments) should be investigated using methods such as thermogravimetry coupled to differential scanning calorimetry and a quadrapole mass spectrometer (e.g. Manning et al., 2005) or RockEval 6 pyrolysis using deconvolution techniques (e.g. Disnar et al., 2003; Sebag et al., 2006). Undoubtedly, fourier transform ion cyclotron mass spectrometry (FT-ICR-MS) will be essential for advanced molecular characterisation of OM. FT-ICR-MS is currently the only technique that resolves the whole range of individual molecules from complex organic mixtures and provides molecular formulas for most of the resolved ions (e.g. Koch et al., 2008), thereby providing the most detailed information possible at present. However, given the amount of data generated, it will be necessary to identify appropriate samples for analysis based on the nested

analytical approach. Further laboratory work should focus on determining the potential rates and products of DOM degradation and identifying appropriate end member signatures for useful biomarker proxies such as lignin phenols.

Microcosm experiments will be essential to measure the decay of humic and iDOM compounds and production of CO_2 in water and soil over time, at the same time linking with biodiversity and (micro)biology. This approach would allow the rates of OM mineralisation, microbial biomass production, and subsequent outgassing of CO_2 to be better constrained with changes in environmental conditions (light/dark, biochemical/photochemical, temperature).

Ultimately, this study shows that only by combining hydrology with geochemistry, microbiology and computer modelling will we fully understand the dynamics of tropical headwater rivers as contributors to the global carbon cycle. Central to this understanding is the identification of the major soil and riverine OM pools and their respective roles in mobilisation, riverine transport and fate of OM at hot spots and during hot moments in tropical rainforest rivers.

6.4 Final thought

Earth sciences are an increasingly large topic of study. The more we learn about the processes and fluxes of various elemental cycles the less we seem to know. The future of our home planet and the sustainability of our bio-diverse ecosystem will only remain if scientists collaborate across disciplines. Science will have to become ever more adventurous to collect field based data that policy makers can utilise to make informed decisions at local, regional and global scales. In return, politicians will have to recognise that the economic risks associated with ‘blue skies’ environmental research is the only way to advance sustainable human interaction with our home.

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